

Preface

Sodium sulfate is the second most common of the water-soluble minerals found in nature, with only sodium chloride being more prevalent. It is also a very large tonnage industrial chemical, and probably first became a useful commodity more than 5000 years ago. There are no records of its first use by ancient civilizations, but massive and fairly pure thenardite (Na_2SO_4 , the mineral form of sodium sulfate) occurred in Egypt near deposits of trona ($\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$), which is known to have been used during that period as a mummifying agent and later in glass and soap. Because sodium sulfate has many similar uses, it is very likely that it also began to be utilized about the same time. Fairly pure sodium sulfate can be easily obtained from many lakes, playas, and outcrops throughout the world, making it logical that some uses for it would have soon developed.

Since the Egyptian period several of its applications, for example, as a substitute for salt (in small amounts), as an animal purgative (in larger doses), and in glass-making, dyeing, and tanning (after being reduced), have been occasionally referred to in historical writings. However, only such low-volume applications remained until the beginning of the Industrial Revolution in 1792, when the LeBlanc process for the production of sodium carbonate began to require it in much larger tonnages. Unfortunately, however, as has so often happened with other innovations, as technology began to be more rapidly developed, this use was soon made obsolete by the advent of the much improved Solvay process. It was not until the Kraft paper pulping process was initiated in the early 1900s that sodium sulfate became a truly large tonnage chemical. Once this process became popular (with sodium sulfate as its main raw material) there was a rush to commercialize many of the world's better-known sodium sulfate deposits.

The history of these early operations is unique, and since many of the deposits that were first worked were located in remote areas, they aided in their areas' development. Also, with this new industry, considerable ingenuity was needed for the efficient production of a salable product, and there was a wide variety of equipment and process innovation. The initial mining procedures were often primitive and involved considerable hand labor, and the processing methods were highly varied and frequently based upon homemade designs. For instance, mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, sodium sulfate decahydrate) has been dried by stacking slabs like

cordwood; decrepitating it to a dry powder in solar ponds; “melting” and drying it in a rotary dryer, on heated rolls, in open pans, or in agitated vessels with flue gas; and melting and evaporating it in many types of multiple-stage vacuum equipment.

Small mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) playas were usually the first deposits exploited, but brine deposits and some outcrops of massive formations of thenardite (Na_2SO_4) and glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$, a sodium–calcium sulfate double salt) were also utilized. In the United States, for instance, the earliest recorded mining operation was in a thenardite–halite (NaCl) deposit, where native people dug a maize of tunnels and left many artifacts behind, including a miner found mummified (by the salt) in a caved tunnel. In Spain small openings in glauberite outcrops on steep slopes were mined with hand tools. The ore was carried down manually and then leached, crystallized, and dehydrated to form sodium sulfate for the LeBlanc process.

As the initial operations developed, matured, and/or were replaced, a very pure product began to be required, and larger and more economic deposits with sophisticated plants began to dominate the industry. The new operations were cheaper to process because they had any or all of efficiency of scale, lower mining costs, other coproducts, proximity to transportation facilities, or purer ore. These more efficient facilities now dominate the world production, and the present large-scale industry has been established.

There are an immense number of sodium sulfate occurrences throughout the world, and a very large number of fairly recently formed small to medium deposits in closed basins. There are also many older sodium sulfate formations occurring either alone or in terrestrial halite deposits. However, there are relatively few (probably fewer than 50) very old, large (100 million to several billion tons of Na_2SO_4), quite pure formations. There has never been a satisfactory explanation of how most of the large deposits originated, and it is difficult to explain why they are in their present form, why they are found only in such limited locations, and often why the sodium sulfate mineral is so pure.

This book considers each of the preceding subjects on the basis of the current operations and an extensive review of the literature. An attempt has been made to describe how sodium sulfate forms and how it is concentrated, deposited, and possibly transformed into the various sodium sulfate minerals. Most of the important deposits and occurrences that have been reported are reviewed and their geological data outlined. The same type of detail has then been given to mining, processing procedures, and the equipment in the world’s present and former sodium sulfate production operations. The major uses of sodium sulfate are described next, followed by industry production and quality statistics. Finally, the most important physical and phase data have been listed and plotted. A large number of pictures, drawings, and references for each of these subjects are included.

Only “natural sodium sulfate” is considered in this book, which focuses on sodium sulfate deposits and how a commercial product is derived from them. The book does not consider the production of sodium sulfate from other chemicals (primarily salt

and sulfuric acid, called “synthetic” sodium sulfate or “salt cake”), recovered as a by-product from the manufacture of other chemicals (such as rayon and chrome chemicals, called “by-product”) or the processing of wastes or wastewater (also “by-product”). The reason for this is that the origin and geology of sodium sulfate deposits are major subjects by themselves, as is the economic extraction of the brine or ore deposits. They require mining or hydrology methods that are unique to each individual deposit, and the initial processing of the ore or brine is also highly varied. These considerations are not encountered with the synthetic/by-product operations, although once either form of sodium sulfate has been put into a fairly pure solution, the final processing steps are similar. The “natural” product accounts for a little more than half of the sodium sulfate that is produced, but over the years this percentage has been slowly increasing.

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Chapter 1

The Origin of Sodium Sulfate and Its Deposits

Next to sodium chloride, sodium sulfate is by far the most common of the naturally occurring saline salts. Each of its most common minerals (thenardite, Na_2SO_4 ; mirabilite [also called glaubers salt], $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$; glauberite, $\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$; astrakanite [also called bloedite], $\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$; and burkeite, $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$) can be found as massive soluble salt deposits, as a major-to-minor component in most of the world's saline lakes or playas, in other saline mineral deposits, or in "alkaline" or saline soils. The minerals may also be found as major-to-minor occurrences in a wide variety of other mineral deposits and geologic formations. Sodium and sulfate ions occur in most waters of all types, groundwater or springs with an excess of sodium sulfate over the calcium sulfate are not uncommon, and a high ratio of sodium sulfate to the other salts occasionally occurs. Consequently, the number of permanent sodium sulfate deposits, or ones that form in the winter from brine in arid-climate closed basins, is very large, but most of them are relatively small.

Since the ancient deposits, or recent playa, saline lake, or brine deposits were usually formed from waters containing many other ions besides sodium and sulfate, it would normally be expected that most of the deposits would be of a mixed-salts type. However, because of the steep solubility curve for sodium sulfate, in the winter and cool evenings mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) is often selectively crystallized from even complex brines. This has resulted in many mirabilite deposits being formed that are both massive and fairly pure, and if it is not the only salt crystallized from the brine, much of the mirabilite is often segregated into fairly pure zones. In many of the deposits some or all of the mirabilite has later been converted to equally pure thenardite, astrakanite, glauberite, or burkeite. The other sulfate salts may also form directly from a mixed-salts brine, but their phase systems are more limited than mirabilite. Finally, glauberite can be formed by the reaction of a strong sulfate brine with gypsum, or any of the sulfate salts (or brine) with a high-calcium water, to also form massive, comparatively pure deposits.

Among the relatively few very large sodium sulfate deposits in the world (greater than 100 million tons of Na_2SO_4), three occur as fairly recently formed playas with a mixture of salts (the Gulf of Kara Bogaz, Turkmenistan; Searles Lake, California; and Laguna del Rey, Mexico). There are some very large mirabilite-brine deposits (e.g., Great Salt Lake, USA; Lake Kuchuk, Russia; and the Aral Sea), and there are large mixed nitrate–sulfate–chloride caliche deposits in Chile. Most of the other very large deposits are ancient buried formations of fairly pure (with little or no other soluble salts) glauberite or thenardite. There are only a few large burkeite or astrakanite deposits, and they occur with other salts. There are also a number of smaller ancient deposits, and some that are less pure than the larger, major ones (including the many glauberite or thenardite deposits in nonmarine halite formations). There have been many theories on where the sodium sulfate came from and the general factors in the origin of the different types of deposits, as summarized below.

THE SOURCE OF SODIUM SULFATE

The sodium ion is a common component of many rocks, and thus is present in all of the waters that have contacted and leached these rocks. The sulfate ion, however, is a fairly rare rock component (except for gypsum/anhydrite), and thus very little of it is leached from the same rocks supplying the sodium ion. Consequently, essentially no sodium sulfate enters spring- or groundwater by the direct leaching of any rocks. It does, however, have a number of quite common sources.

Gypsum: Calcium Precipitation

First, and what is generally agreed to be the dominant sulfate source for all of the world's large sodium sulfate deposits, is the leaching of gypsum or anhydrite. These minerals are relatively common and fairly soluble, thus supplying a significant amount of calcium and sulfate to many waters. If this water evaporated directly it would redeposit all of the gypsum, but there are two methods by which sodium sulfate can result from leached gypsum. The most prevalent method but probably the least important for the large deposits, is due to the fact that all waters absorb some carbon dioxide from the air to produce small amounts of carbonic acid or bicarbonate ions ($\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+$). Larger amounts are absorbed if the water is slightly alkaline, such as when it has leached sodium (and/or potassium), and with it primarily weakly acidic anions (such as silicates, hydroxides, or borates instead of the strongly acidic anions chloride and sulfate). Much more carbon dioxide can be absorbed, and there will also be carbonate ions present in highly alkaline water such as that found in many hot springs, or when alkaline waters evaporate. Some geothermal or other deeply originating water may also initially contain considerable bicarbonate and/or carbonate.

When neutral or acidic groundwater evaporates much of the absorbed carbon dioxide is initially driven off, but in alkaline waters (with $\text{pH} > 7$) an equilibrium is established between carbon dioxide and the bicarbonate and carbonate ions. Greater evaporation leads to increasing concentrations of the carbonate ion. The carbonate formed by this equilibrium thus allows about half of the absorbed CO_2 (or initially present bicarbonate; $2\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{CO}_2 + \text{H}_2\text{O}$) to precipitate with calcium, and then magnesium in the water, along with any carbonate ions that were originally present. This precipitation occurs early in the evaporation cycle, forming calcite (and dolomite or magnesite, depending on the ratio of calcium to magnesium in the water).

With most waters this only removes a small portion of the calcium that may have been in the water from dissolving gypsum or other rocks, but whatever the amount removed, the remaining ions can then become a sodium or other cation (Mg, Al, Fe, etc.) sulfate. For mildly to strongly alkaline waters, or ones that have not contacted much gypsum, some to most of the calcium may be precipitated, allowing the water to become a dilute sodium sulfate, mixed sodium sulfate–sodium carbonate, or sodium carbonate solution. As an example of this reaction, in the very large Madrid, Ebro, and Calatayud Basin deposits of Spain this appears to have been the source for a small part of the sodium sulfate in the basins, since there are scattered formations of chert, opal, silica, and other silicates (and corresponding amounts of calcite) around the edges of the basins (Orti *et al.*, 1993). This is indicative of highly alkaline spring waters, since only such waters dissolve enough silica to form significant deposits of these minerals. The silica (or silicates) would have slowly precipitated as the spring waters entered the closed basins' lakes or playas, while the calcite would have precipitated immediately with the calcium in the area's high-gypsum groundwater. However, the amount of silicates is very small compared to the sodium sulfate minerals present, so it was probably only a minor sodium sulfate source.

Gypsum: Ion Exchange

Again, it is generally agreed by most experts in this field that a second and more important transformation of some of the dissolved gypsum occurs by the ion exchange of calcium with the sodium contained in various clays and other rocks. Most clays and zeolites have some ion exchange capability, and divalent ions such as calcium are much more strongly retained by them than the monovalent sodium. However, since ion exchange works on a mass action basis, strong solutions of either ion will cause the replacement of the other. Thus, because of the prevalence of concentrated sodium chloride solutions in nature (such as in the evaporation of seawater, and in most closed lacustrine basins), as the associated clays or zeolites were formed by breakdown, weathering, or chemical reactions with their parent rocks, they would commonly be in the sodium form. Consequently, if these clays or zeolites were later contacted or washed from their formations by a gypsum-containing

water into an arid-climate, closed basin, some of the calcium would replace the ion exchanger's sodium to form sodium sulfate.

This combination of nearby gypsum and large amounts of sodium-form ion-exchangeable clays or zeolites appears to be a necessary combination to explain the sodium sulfate content of all of the large sodium sulfate deposits, as well as many of the smaller ones. The gypsum and clay/zeolite precursors would have most often originated near each other, such as in the same marine formation. In each of the sodium sulfate deposits' lacustrine basins the non-ion-exchanged calcium would reprecipitate as gypsum, possibly becoming a major component in the formation.

Other Sources

Sodium sulfate may also be produced from the sulfuric-sulfurous acid formed by the oxidation of sulfur, pyrite, or other sulfide minerals. Sulfur and sulfides, when exposed to the air or certain bacteria, are oxidized to sulfur dioxide that eventually combines with water to form sulfurous acid, which may be further oxidized and reacted with water to form sulfuric acid. Both acids then react with rocks that they contact to form a series of metal sulfites or sulfates, but most of the heavy metals that might be leached soon reprecipitate from the groundwater as carbonates, hydroxides, silicates, phosphates, etc. The sulfites also quickly oxidize (by air), and sodium sulfate thus usually becomes a major end product from these reactions. A similar set of reactions occur from rainwater that absorbs sulfur dioxide from the air, or to a lesser extent hydrogen sulfide from marshes (formed by sulfate reducing bacteria), volcanoes, some hot springs and geysers, etc. The hydrogen sulfide in time oxidizes to sulfur dioxide. Finally, the sulfate ion (primarily as sodium sulfate) is a major component of seawater spray that enters coastal regions in considerable quantity. Each of these minor sources are known to have contributed to the formation of some sodium sulfate deposits.

Another source could be deeply originating springs with a water high in sodium sulfate and low in other salts. However, there are essentially no such springs in the world today, and it seems highly improbable that there were many in prehistoric times. The limited number of large sodium sulfate deposits would appear to have required a more complex source than pure springs, or merely the leaching of gypsum and "rocks."

An Ion-Exchange Example

It is difficult to trace the association of the probable precursor clays and gypsum in most of the large deposits, but in one case, the very large number of Canadian-U.S. prairie sodium sulfate lakes, there is a very close association. The deposits are all located in depressions formed in fairly porous glacial till that last spread over the area about 12,000 years ago. Within the till are small-to-substantial amounts of gypsum from the underlying marine sediments, and large quantities of "boulder clay,"

presumably from the shales in the marine formations (to have placed the clay in the sodium form). There are also very small amounts of pyrites in the till (Edmunds, 1957). Most of the runoff and springwater in the area has only a modest concentration of sodium sulfate and gypsum, and fairly normal amounts of the other common salts. In the mirabilite deposits there are very low to normal amounts of calcite and gypsum that precipitated during the early evaporation period in the closed basins. There are also areas among the sodium sulfate lakes where there is considerable sodium sulfate in the soil, usually in "black (or brown) clay." Finally, oxygen and hydrogen isotopic data has shown that the brine in the sodium sulfate lakes originated primarily from meteoric, near-surface water, and not from a deeper source (Kelley *et al.*, 1998).

It would be logical that the large excess of clay (that probably was originally in the sodium form) in this deposit area compared to the amount of gypsum, and the wide distribution of the clay throughout the groundwater leach zone, has led to fairly complete ion exchange of the groundwater's calcium (from the slowly leaching gypsum) for the clay's sodium. The very dilute sodium sulfate water that is formed has slowly concentrated in the closed basins, and the selective mirabilite crystallization during the area's cold autumn, winter, and spring has allowed the other salts to preferentially seep away (i.e., the other salts can seep all year, the sodium sulfate only for the period when it is not a solid phase, or less than one-fourth of the time). This preferential seepage phenomenon can be seen occurring today in Chaplin Lake, Canada (as well as the other Canadian and Turkish commercially operated sodium sulfate lakes), where all of the reject brine from their solar/glauber salt-forming ponds is returned to the lake, and yet after more than 50 years of operation the content of sodium chloride, magnesium, potassium, bromine, etc., in the lake brine has not appreciably increased. Also at Chaplin Lake there are indications of a new supply of sodium sulfate entering the lake as a very dilute mixed-salts runoff and groundwater, since the sodium sulfate reserves were estimated at 3 million tons in 1954, more than 3 million tons have now been produced, and 2 million tons of recoverable product are estimated to be still present.

It would thus appear that this origin theory fits the data and observations gathered on these deposits quite well, and there are no other theories with any physical support. Since this deposit is so large (considering all of the lakes together), and apparently still growing, it may present a reasonable example of both the origin of sodium sulfate, and the formation mechanism of some of the world's other large sodium sulfate deposits.

MIRABILITE

As noted previously, mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) can be readily crystallized from fairly concentrated brines in the winters of all climates of the world, and in the cooler evenings of most climates. In very cold winter climates it can also crystallize from

relatively dilute brines, and even seawater. Thus, in closed basins where water can accumulate and evaporate to a fairly high concentration in the summer, and where there is an excess of sodium sulfate in the water, mirabilite will usually deposit to at least some extent in the following fall and winter. If the amount of other salts with a steep solubility curve (such as natron [$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$], epsomite [$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$], or borax [$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$]) is limited in the water, the mirabilite will be quite pure. The mirabilite can crystallize on a lake's surface or bottom, throughout a shallow playa, in or just beneath the playa's surface crust, and in the near-surface sediments. If the deposit is sufficiently massive or becomes covered by a concentrated brine or sediments, or if it is in a density-stratified lake, some or most of it will survive the dissolving tendency of the next spring's rains and/or playa flooding, and a permanent deposit will form and grow. In lakes this tendency will be assisted by mirabilite's low density, allowing some of the newly formed crystals to float and be driven by the wind as "rafts" (that occasionally form up to 0.5 m thick) onto the shore, where their chance for survival is somewhat improved by burial and/or their thickness (without agitation their endothermic [cooling] effect when dissolved and the high-density brine that is formed can insulate the mirabilite lower in the mass).

There are literally thousands of massive and pure mirabilite occurrences in the world today, existing as (1) the only mineral deposit in a playa or lake (e.g., the Canada–Montana–North Dakota prairie lakes or playas; Great Salt Lake, Promatary Point), (2) as pure deposits in isolated zones of playas with other mineral deposits (e.g., Rhodes Marsh, Nevada; Laguna Salinas, Peru), or (3) as pure intermittent winter deposits in sulfate-containing lakes (the Aral and Caspian Seas; Great Salt Lake, southeast shore; Gulf of Kara Bogaz). It is fairly easy for each of these deposit types to become massive (even without a subsiding basin) and remain very pure. However, mirabilite is not a stable mineral for long-term survival or deep burial because of its low melting point, high solubility, and thus easy reactivity. The mirabilite most commonly transforms into equally pure and massive beds of thenardite, glauberite, astrakanite (bloedite), or burkeite, minerals that are somewhat more stable. The transformation into thenardite also occurs readily by heat, evaporation, or the presence of concentrated salt solutions.

Seepage

All lakes and playas undergo a continuous but variable amount of seepage, with some brine always being lost. In very tight basins such as Searles Lake this loss may be almost negligible, but in most basins it varies from a very small amount to a considerable flow. As a consequence, if one of the brine components in a lake or playa is in a solid phase (such as mirabilite) for some to much of the year, the other components are disproportionately lost by this seepage process. Thus, even if dissolved again the next spring, the easily crystallizing phase steadily becomes a higher proportion of the water's salts, allowing even purer deposits of mirabilite to form. The colder the climate, the more exaggerated this effect becomes, as is seen in

Antarctica, Canada, and Central Russia. In warmer climates where the fraction of the year that the mirabilite can deposit is shorter, it takes longer for this effect to develop, and the percentage of predominately sodium sulfate lakes is smaller.

Because of this phenomenon, any water that enters a closed basin with an arid climate and contains some sodium sulfate, no matter how small its original fraction or the amount of other salts, can become a fairly pure mirabilite deposit. This is seen in the Canadian–U.S. prairies with the many glacial basins in porous glacial till and boulder clay. The lakes have fairly thin mud bottoms over the porous glacial till, the area has an arid climate and very cold fall, winter, and spring. Thus, even though the entering spring- and groundwater is quite dilute and has a fairly low ratio of sodium sulfate to the other salts, after the lake waters have been concentrated by summer evaporation (and usually some halite and thenardite crystallized) mirabilite can fairly selectively crystallize almost completely from the remaining brine for about three seasons of the year while the other salts slowly seep away. This cycle of seepage, along with flooding, evaporation, and selective crystallization, thus allows the sodium sulfate to slowly concentrate.

Other Salts

When there are appreciable amounts of other salts in the entering water that also have a steep solubility curve, such as sodium carbonate (to form natron), magnesium sulfate (to crystallize epsomite), or borax, then these salts will also concentrate with or in place of the sodium sulfate if its ratio to the other salts is low. Depending on the concentration of the other salts, this can form a mixed-salts deposit, or any one or more of the other salts can preferentially concentrate. Thus, in Owens Lake, California, in the winter natron, mirabilite, and borax all form, and since sodium chloride is dominant there has been no appreciable concentration of any of the salts in its 3500 years of existence. In Metiskow Lake in Alberta, Canada, both sodium sulfate and sodium carbonate have concentrated, as have sodium sulfate and magnesium sulfate in Muskiki Lake in Saskatchewan, Canada. In lakes in British Columbia, Canada, sodium carbonate is the dominant concentrating salt, although there are some lakes that contain primarily sodium sulfate and others with high magnesium sulfate. In the Okanogan Plateau, Oregon–Washington, about an equal number of dominant sodium sulfate, sodium carbonate, and magnesium sulfate lakes have formed by this effect.

THENARDITE

The most common method for the formation of thenardite (Na_2SO_4) in essentially all high-sulfate playas is by its crystallization during capillary evaporation in the surface crust, and/or the summer dehydration of some or all of the mirabilite in the crust or near-surface deposits. In the former case the thenardite is usually present

in a mixture of salts, and in the latter case variable amounts of mirabilite may remain with it. Fairly pure deposits of thenardite may also be formed from a high-sulfate brine in a shallow lake by direct crystallization in the summer from warm brine ($>9^{\circ}\text{C}$ from a NaCl-saturated solution; $>32^{\circ}\text{C}$ from a pure sodium sulfate brine). Finally, buried mirabilite deposits may be converted to thenardite by a high-NaCl brine's salting-out effect, and/or when "melted" at temperatures above $9\text{--}32^{\circ}\text{C}$.

Examples of Deposits

The preceding mechanisms have been reported many times in present-day playas or lakes, such as at Lake Kuchuk in the Volga region of Russia. During the summer as the brine evaporates and the lake level drops, the brine is heated and becomes saturated with NaCl. This converts the winter-formed mirabilite lying at the bottom of the lake into thenardite, with a thin bed of insolubles and organic matter (forming varve layers) also being deposited before or during the conversion (Stankevich *et al.*, 1990). Thenardite forms in a slightly different manner in lakes of the Kulunda steppe region of Russia, where it deposits in the summer between the playa's mud bottom and a surface crust of halite. The sodium sulfate source is the groundwater leaching of mirabilite that has formed in the winter above, below, or in the mud layer. As this brine collects above the playa's mud surface or rises through the mud, it is contacted by the descending NaCl-saturated brine. In this warmer upper layer, with capillary evaporation also taking place, the thenardite slowly crystallizes, often forming permanent, and sometimes thick, pure beds (Stankevich *et al.*, 1990). In Rhodes Marsh, Nevada, thenardite has formed as a massive body under and within a halite deposit, and adjacent to or under a thick layer of mirabilite. In some other playa/lakes the thenardite deposits lie on top of massive halite.

A somewhat similar thenardite formation mechanism for warmer climate high-chloride and medium-sulfate brines has been noted in Australia, Egypt, India, and South Africa. For instance, in South Africa at the Grootwitpan solar salt operations the brine is evaporated to deposit both salt and mirabilite (the former crystallizes for seven months per year during the days, while the latter forms in the evenings). The residual brine is then drained, and the ponds allowed to stand idle for a brief period, causing much of the solar radiation to be captured by the interstitial brine, thus heating it. The warmer temperature dissolves much of the sodium sulfate, and the heavier, saturated brine that is formed then sinks to the semi-impermeable clay beneath the salt. There, with continued capillary evaporation the thenardite crystallizes into thick, permanent beds of fairly pure thenardite (Sutherland, 1993). At the Didwana salt ponds in India the seepage through the pond bottoms is so great, and the entering sulfate content low enough, that as the brines concentrate very little sodium sulfate crystallizes in the salt that is being deposited. Instead the strong brine seeps through the salt and has formed a thick ($>1\text{ m}$) deposit of quite pure thenardite, probably by a mechanism of first being cooled to form mirabilite, followed by salting-out to produce thenardite (Spencer, 1944).

Despite these and many other examples of thenardite being formed in present-day playas, its mechanism of formation in the world's large, ancient deposits is still somewhat uncertain. There are many deposits with old pure thenardite and little to no glauberite, such as at Cerro Blanco, Argentina; Bachaduachi, Mexico; Salton Sea, California; Camp Verde, Arizona; some in China and the former Soviet Union; and in many terrestrial halite deposits. None of the deposits contain much if any gypsum, so there would have been no calcium source in the deposit for a glauberite reaction. Also, perhaps there was no (or a limited amount of) high-Ca groundwater in the basin, or the groundwater was partially or totally sealed from most of the mirabilite. Many of today's large recent thenardite or mirabilite deposits are in clay-filled basins, protected from groundwater.

GLAUBERITE

Glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$) is found as the principal sodium sulfate mineral in a number of very large deposits, both alone and mixed with astrakanite, or interbedded or underlying thenardite. It is frequently found with lacustrine halite deposits, smaller amounts are often found in saline playas, and some is occasionally present in other soluble sodium sulfate or soluble-salt deposits or occurrences. It is quite soluble in water, and fairly soluble in sodium chloride solutions, thus requiring a >20–25% sodium sulfate solution to precipitate when there is less than 5% sodium chloride present, and $>\sim 10\%$ Na_2SO_4 when the solution is saturated with NaCl. These are very concentrated solutions and can only be found near the end of a basin's evaporation cycle. Also, when a high-sodium-sulfate (and usually high-sodium-chloride) water or brine is evaporated in a closed basin, only very small amounts of glauberite could be directly crystallized with its own calcium content (if any at all), since most brines contain <800 ppm Ca in the latter periods of the evaporation sequence. However, glauberite can be readily formed by a high-sodium sulfate brine (with concentrations as noted above) contacting gypsum, or when a high-calcium water (in limited supply) contacts mirabilite, thenardite, astrakanite, burkeite, or the high- Na_2SO_4 brine formed by these minerals.

Examples of Glauberite Formation: Australia

Many investigators have noted the formation of glauberite by these reactions. For instance, Arakel and Cohen (1991) observed the crystallization of glauberite in desert playas (in the Northern Territory, Australia) by the summer reaction of a concentrated high- Na_2SO_4 , low-other-salts brine with (1) gypsum (thus replacing it) in a wet vadose zone (up to 1 m thick between the surface and the water table), and (2) high-Ca groundwater reacting with the brine (or mirabilite) in a phreatic zone (below the water table). In the latter zone the glauberite was concentrated close to the water table surface, and in the vadose zone the glauberite grew first on the edges

of gypsum crystals, then the faces, and progressed inwards. In this study the aquifer brine was too weak to allow either reaction to occur, but because of capillary evaporation the most complete gypsum replacement was near the surface of the playa. Also, mirabilite would have formed during the winter and cool evenings near the water table surface, and as it later dissolved it would have leached gypsum, increased the brine concentration, and directly precipitated glauberite. It could have also been a direct reactant with the groundwater.

The Former Soviet Union

A much more comprehensive study of glauberite formation has been made by Grokhovskii (1978), generalizing on observations from a large number of desert lakes or playas with many brine types in the former Soviet Union's Asian (southern) provinces, including the Gulf of Kara Bogaz (with its reported 2–4 billion tons of glauberite in fairly thick beds). The glauberite was usually present as “pulpy masses, in lenses and layers, and in salty bottom deposits.” It was much less frequently found as larger crystals or crystal clusters. The glauberite could be quite pure, or in pulps with ~50% halite, gypsum, clay, various Mg and Ca carbonates, and organic matter. When there was a halite crust on the playa, often with some thenardite, mirabilite, or astrakanite, there frequently was 10–50 cm of pasty glauberite beneath it. In dryer playas the glauberite was often interbedded with halite, thenardite, astrakanite, or mirabilite.

In the playas with magnesium in the brine, the spring runoff waters would dissolve some or all of the previously crystallized salts, and then evaporate in the summer to deposit a layer of halite and epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) over any residual mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). When the surface water was nearly completely evaporated, a high-Mg residual brine would begin to seep through the underlying salts, converting the mirabilite and epsomite into astrakanite ($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$), and calcite (CaCO_3) or dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) into magnesite (MgCO_3). Later, when most of the residual brine was gone, and high-Ca ground water from the surrounding area would again begin to flow into the subsurface of the playa (or if the groundwater entered from a higher elevation), the upper surface of the astrakanite would react to form a pasty glauberite mass.

If the original lake waters were low in magnesium, then glauberite would form between the halite and mirabilite. As this conversion proceeded some crystals of glauberite would also form in the lower, more porous zone of the halite by a direct reaction of the sulfate in the residual brine with the high-Ca water. The warm groundwater would also convert some of the mirabilite or astrakanite into thenardite and dissolve the remaining halite, and with a sufficient flow only a bed of thenardite would remain under a mass of pasty and crystalline glauberite. If the groundwater flow continued, glauberite could also form under the thenardite at its expense until all of the thenardite was gone, and eventually the glauberite would also disappear. However, normally much of the glauberite survived this evolutionary cycle, and

often some or much of the halite. As the conversion process continued the pasty glauberite would slowly change into a more massive and solid form, but since some of the mirabilite would also dissolve as the remainder converted to astrakanite and/or glauberite, void space would be left in the glauberite mass, and it would remain porous until sufficiently buried to close the voids. A similar situation would exist in the overlying halite because of its original epsomite and thenardite content, and it would also be porous.

In addition to the general case discussed above, glauberite could crystallize in several other locations. A pasty layer may form in or near the surface crust from having transformed thenardite, mirabilite, astrakanite, or epsomite. Later a thenardite layer may form over this pasty glauberite or under the halite as some of the glauberite is dissolved and the brine recrystallizes. When the playa re-floods some or all of the thenardite usually dissolves, but much of the glauberite remains. If, however, there is not a large new water input, the thenardite usually remains at the expense of the glauberite. In various of the lakes and playas that were studied (such as Lake Azhbulat and the Gulf of Kara Bogaz), some glauberite also formed by the reaction of high-sulfate brine with gypsum, or by the direct reaction of mirabilite or end-liquor brines with intruding high-Ca groundwater, thus forming more massive and bedded deposits. Zhu and Hu (1989) have summarized their similar findings on the location of glauberite in Chinese playas, as shown in Fig. 1.1.

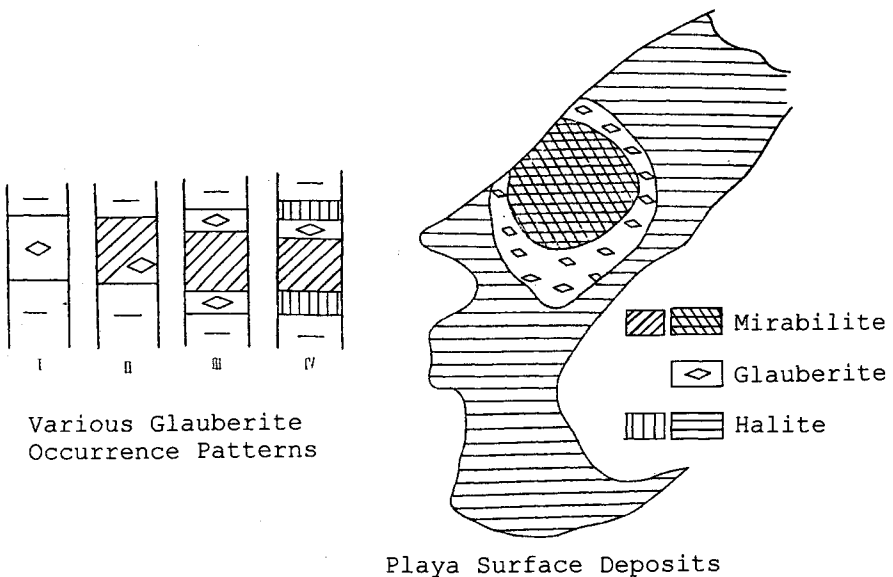


Figure 1.1 Typical formation of glauberite in a Chinese playa lake. (From Zhu and Hu, 1989.)

Gulf of Kara Bogaz Deposit

The preceding descriptions fit the Gulf of Kara Bogaz's massive glauberite deposits quite well. During relatively dry seasons large amounts of mirabilite crystallized in the winter from the more concentrated brine in the outer sections of the Gulf (before the straits to the Gulf were blocked). Much of it fell to the floor of the shallow lagoon, but the crystals that floated blew to the shores and formed large deposits (some of which were harvested in the early 1900s). In the spring when the lagoon reflooded, residual concentrated brines kept much of the mirabilite from dissolving, and later in the next summer halite with some epsomite deposited over the mirabilite. During the following winter the process was repeated, and eventually the alternating halite–mirabilite layers were deep enough to be effected by inflowing high-Ca groundwater, converting some of the mirabilite with the epsomite to astrakanite, and then both to glauberite. The groundwater near the shore (Zone 1 of Figure 3.32) in time converted most of these salts to glauberite and slightly diluted the strong residual brine, leaving high sodium sulfate mineral and brine compositions (Kurilenko *et al.*, 1988).

The same thing happened in the shoal area of Zone 3, except here the additional leaching from unsaturated surface brine also dissolved most of the halite. In the other zones a combination of surface and subsurface leaching left a mixture of halite, glauberite, and astrakanite. In each zone the mineral layers were porous and filled with brine. Eventually a wetter period would occur and the brine would not become concentrated enough to crystallize (or at least preserve) mirabilite and halite, and the thick in-between layers of gypsum, carbonates, and clay would form. Later a dryer cycle would return, and over the past ~500,000 years four thick glauberite-containing beds have formed.

Kosolov *et al.* (1974) and Chilingar (1956) also noted that since the Gulf of Kara Bogaz had been alternately flooded and dried over a very long period, gypsum was deposited throughout its sediments as 0.1–0.2 mm to 5–6 m thick gypsum-rich layers (it could deposit after only a 6% evaporation of Caspian Sea brine). Consequently, in zones where strong sodium sulfate brine could form by evaporation or leaching of other soluble sulfates, and the temperature was greater than ~10°C, some or all of the gypsum could be replaced by glauberite.

Formation Mechanism for Other Large Deposits

From the references noted previously, it appears to be well documented that glauberite deposits can form by (1) direct precipitation from a high-sodium-sulfate brine by an intruding high-calcium water; (2) reaction of a high-sodium sulfate-brine with gypsum; and (3) reaction of a high-Ca water with mirabilite, thenardite, or astrakanite. It has also been demonstrated in the laboratory that a high-sodium-sulfate brine can precipitate glauberite directly from its own calcium content, but this is a trivial deposit-forming mechanism since the amount of calcium that is present is so small (<0.1%), and the allowable concentration range so narrow. Among

these mechanisms it would appear that the conversion of mirabilite could most easily explain the very thick, very pure glauberite deposits that occur in Spain and elsewhere. There are many locations known today where very thick, shallowly buried mirabilite deposits exist, and if they had been codeposited with gypsum, then a high-Ca groundwater at a temperature above 10–27°C (depending on the amount of NaCl present) could convert them to glauberite. Once started at the edge of the deposit the reaction would be self-sustaining, since the former water of hydration would be saturated with Na_2SO_4 , and as it leached some of the gypsum glauberite would form. The residual brine would then leach more mirabilite and gypsum, and the reaction would very slowly continue until all of the mirabilite was consumed. The water-of-hydration brine would eventually seep away, just as with gypsum dehydrating to anhydrite during deep burial. Presumably in the deposits containing magnesite with the glauberite (indicating the presence of a residual high-Mg brine), at least some mirabilite must have been converted to astrakanite, and then it was also changed to glauberite by this same dehydration–leaching–reaction mechanism. Very little astrakanite remains in the glauberite–magnesite deposits in Spain and Turkey, but there are limited amounts in Tien Shan (Kyrgyzstan), and major amounts in the Laguna del Rey (Mexico), Kara Bogaz (Turkmenistan), and Bertram (USA) deposits.

As an alternative mechanism, in some deposits perhaps a brine that was high in sodium sulfate and low in other salts reacted with thick and pure gypsum beds to form the glauberite. Observations on current playas and the enterolithic structure of some of the thinner ancient deposits indicate such a reaction. However, such brines are quite rare, and there would have to have been a long-lasting and consistent concentrated supply. The deposits could not contain magnesite unless astrakanite was also present, since any brine that could form magnesite could more easily form astrakanite. Also, the probability of the glauberite being very pure would be low, since normally carbonates and clays deposit with gypsum, and even if the gypsum were pure, large amounts of it should have remained unreacted because of the low permeability of the deposit. This reaction must have accounted for some of the large, ancient deposits, but it is probably limited to the thinner beds of less pure glauberite.

Isotopic Studies

Further indications of the source of glauberite in the Madrid, Ebro, and Calatayud Basins in Spain and at Tien Shan, Kyrgyzstan, have been made by isotopic studies. The heavy sulfur (^{34}S) and oxygen (^{18}O) in thenardite, glauberite, polyhalite, and gypsum have been determined (Table 1.1). These values are of interest since in any reaction or physical change, the lighter isotopes (in this case ^{32}S and ^{16}O) are more active, and thus are slightly preferentially included in the reaction or change. The material left behind thus increases in the heavier ^{34}S and ^{18}O isotopes. In examining the isotopic data for these deposits it is indicated that the gypsum in the basins with the nonmarine sodium sulfate deposits recrystallized from leached marine

Table 1.1

Comparison of the Isotopes of Sulfur ($\delta^{34}\text{S}$) and Oxygen ($\delta^{18}\text{O}$) in Glauberite, Thenardite, Polyhalite, and Gypsum in Selected Deposits^a

Reference ^b	$\delta^{34}\text{S}$			$\delta^{18}\text{O}$	
	1	2	3	1	2
Madrid Basin, Spain					
Thenardite	15.0	—	—	17.6	—
Glauberite	15.2	—	—	17.5	—
Polyhalite	14.6	—	—	16.6	—
Gypsum	16.3	16.6	—	17.2	15.4
Anhydrite	15.6	—	—	17.9	—
Average thenardite, glauberite, polyhalite		(14.9)		(17.2)	
Average gypsum, anhydrite		(16.2)		(16.9)	
Ebro Basin, Spain					
Glauberite	12.5	—	—	17.9	—
Gypsum	13.0	13.0	14.9	18.8	15.6
Average gypsum		(13.6)		(17.2)	
Calatayud Basin, Spain					
Gypsum	—	15.0	—	—	16.3
Triassic Gypsum, Spain	—	13.4	14.7	—	11.8
Average Gypsum		(14.1)			
Cretaceous Gypsum, Spain	—	18.2	—	—	14.4
Tien Shan, Kyrgyzstan (ref. 4) $\delta^{34}\text{S}$: Glauberite 12.8; Permian gypsum 18					
Atmospheric SO_2 $\delta^{34}\text{S}$ (ref. 3): 0–5					
Fresh water $\delta^{34}\text{S}$ (ref. 3): 5–10					
Sulfide minerals $\delta^{34}\text{S}$: –50 to +8					

^a All values are positive unless noted.

^b References: 1, Ordonez and Del Cura (1992); 2, Utrilla *et al.* (1992); 3, Birnbaum and Coleman (1979); 4, Chukhrov (1972).

gypsum in the surrounding formations. The Ebro and Calatayud Basins are entirely surrounded by watersheds containing Triassic marine sediments, with the average Triassic gypsum's $\delta^{34}\text{S}$ value being 14.1, while the Ebro basin's gypsum was 13.6, and the Calatayud basin 15.0. The Madrid Basin has a watershed with three sides of Triassic and one (the east) of Cretaceous marine rocks (with its gypsum's $\delta^{34}\text{S}$ 18.2). The average Madrid Basin gypsum and anhydrite $\delta^{34}\text{S}$ values were 16.2, or a blend of the Triassic (14.1) and Cretaceous (18.2). In each basin the $\delta^{34}\text{S}$ values are sufficiently similar to indicate that leached marine gypsum flowed into the watershed and was the source of the later recrystallized gypsum in the glauberite or thenardite deposits (the sulfate's $\delta^{34}\text{S}$ in nonmarine water is 5–10; in seawater for many other geologic periods ~20; sulfides are –50 to +8).

In the Madrid Basin the average $\delta^{34}\text{S}$ of the glauberite, thenardite, and polyhalite is 14.9 and its gypsum 16.2. In the Ebro Basin the glauberite is 12.5 and the gypsum 13.8; at Tien Shan, Kyrgyzstan, the numbers are 12.8 and 18. Again the values are fairly similar, but the sodium sulfate minerals are always slightly lower, indicating an additional fractionation of the sodium sulfate. This could have occurred by mirabilite having been the first soluble sodium sulfate mineral crystallized, and the precursor to the glauberite and thenardite. This would have given the sodium sulfate slightly lower $\delta^{34}\text{S}$ values. Then later, a strong NaCl solution (or compaction and burial) would have changed the mirabilite to thenardite, or intruding high-Ca groundwater would have changed the mirabilite to glauberite (with or without the intermediate formation of astrakanite). In both cases, first the mirabilite would have been totally dissolved, and then the thenardite or glauberite recrystallized with additional fractional crystallization as the heavier residual sodium sulfate left with the water of crystallization. With the glauberite, if gypsum had been its precursor, or with direct precipitation from brines, the sodium sulfate's $\delta^{34}\text{S}$ should have remained essentially identical to that of the gypsum, which it did not. The later formation of polyhalite from gypsum by high-magnesium and -potassium end liquor would have somewhat similar opportunities for fractional crystallization.

The much higher values of $\delta^{18}\text{O}$ in the lacustrine salts than in the marine gypsum appear to have been caused by a partial oxygen exchange between the sulfate ions and the water, as has been observed by Rafter and Mizutani (1967) in several sulfate-containing waters. Their studies indicated that the isotopes of oxygen are fractionated along with the sulfur in a physical or chemical change of sulfate ions, but only after the sulfate's oxygen has first moved in value toward the same number as the $\delta^{18}\text{O}$ in the water (indicating an oxygen exchange). In this case there would have been an increase in the water's $\delta^{18}\text{O}$ during the considerable evaporation required before the sulfate salts could crystallize, so the water's (and thus the sulfate's) $\delta^{18}\text{O}$ would have increased. Had the $\delta^{18}\text{O}$ increase been from sulfate-reducing bacteria preferentially attacking the lighter sulfate and oxygen (as shown to occur by Mizutani and Rafter, 1969), then the $\delta^{34}\text{S}$ would also have increased, which it did not. Also, such bacterial reduction almost always affects only a minor fraction of the sulfate that is present in such a large deposit.

Impurity Studies

A further indication of mirabilite having been the precursor mineral to glauberite or thenardite deposits is given by trace mineral analyses. In the data of Orti *et al.* (1979) for Spain's FMC Foret mine, the lithium content of polyhalite is only a little lower than that of anhydrite. This is as expected, since polyhalite normally forms by the reaction of strong end liquors with gypsum, anhydrite, or glauberite (further indicated here by the presence of many pseudomorphs of polyhalite after these minerals). However, the lithium contents of glauberite and thenardite are 100–1000 times lower than in gypsum/anhydrite, indicating that they did not form from these

minerals, or by direct precipitation from the evaporating water (as did the gypsum). The same differentiation occurs with strontium, which is nearly the same in polyhalite and anhydrite, but in glauberite and thenardite it is 2–70 times lower.

The Sodium Source

As a final consideration, since marine gypsum appears conclusively (from the isotopic studies) to have been the principal source of the sulfate ion in these massive deposits, it is likely that only an ion exchange of calcium for sodium by marine clays or zeolites (that were also in the watershed) could account for the majority of the sodium in these deposits. There is no indication of extraordinary prior carbonate deposition (to match the sodium sulfate minerals in size) that would have been present if carbonate precipitation supplied most of the deposit's sodium. There is also no indication of the presence of high-sodium-sulfate springs. The lack of sodium sulfate minerals in the similar nearby nonmarine gypsum-containing basins, or others throughout the world, could perhaps be explained by the lack of sufficient amounts of suitable clays (or zeolite) in their watersheds, or, of course, by their not being adequately closed or structured to have allowed the extensive evaporation required for precipitation of sodium sulfate, or for its survival once formed.

ASTRAKANITE AND BURKEITE

These two minerals are very common soluble sulfates, with the astrakanite ($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$; also called bloedite) being found in many high-sulfate, magnesium-containing playa and lake deposits. Burkeite ($2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$) is equally common in the high-carbonate deposits, and both are found in many other geologic situations. Neither mineral occurs as a pure isolated, commercial sodium sulfate deposit, but both have been or are contributing to commercial mixed-salt operations. Astrakanite is a major component in one area of Tien Shan (Kyrgyzstan), and in the Gulf of Kara Bogaz (Turkmenistan) and Laguna del Rey (Mexico) deposits. In the two latter cases the natural leaching of the deposits' minerals provides a high-sulfate brine to be processed. In a similar manner at Searles Lake (California) the leaching of lake salts (including burkeite and thenardite), followed by plant evaporation, produced burkeite that was converted into sodium sulfate. Several of the world's other large burkeite deposits are also commercially operated (or have been studied; e.g., in China and Namibia) for their sodium carbonate and sulfate content.

ACCOMPANYING MINERALS: DOLOMITE AND MAGNESITE

Dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) and/or magnesite (MgCO_3) are often found in soluble sulfate deposits. For instance, dolomite is the predominant carbonate mineral found in the soluble sulfate zone of Spain's Ebro Basin, with magnesite only being present

in its Alcandre-Arrubal area's glauberite beds. In Spain's Madrid Basin, however, magnesite is the dominant carbonate mineral throughout the thenardite and glauberite zones. In many other soluble sulfate deposits at least some dolomite and/or magnesite are present, and often as important constituents.

Since dolomite is such a common mineral many studies and observations have been made on the factors involved in its formation in sedimentary deposits. However, magnesite is much less common and well studied, although it is known that magnesium carbonate can precipitate directly from evaporating (or CO₂-rich) waters alone or with calcium in all proportions (the mixtures are called protodolomite until they are near the stoichiometric ratio of dolomite). Magnesium carbonate tends to deposit after most of the calcium has been precipitated, but there are still carbonate ions in the water and the magnesium is slightly more concentrated. An example of this is in the Gulf of Kara Bogaz, where the sediments near the Caspian Sea entrance to the Gulf contain about 15% calcite, but farther inland this changes to 10% hydromagnesite (MgCO₃ · 2H₂O; Kosolov *et al.*, 1974).

As an even more common method of forming dolomite or magnesite in large deposits, high-magnesium-chloride or -sulfate end liquors (from the extensive solar evaporation of waters) can replace the calcium in calcite with all ratios of magnesium (this is called the dolomitization reaction). Magnesium chloride is very soluble, and thus is often concentrated in the end liquors of many evaporating water or brine bodies. Many brines that have evaporated sufficiently to crystallize sodium sulfate would therefore be left with a fairly strong magnesium chloride solution. When this heavy, high-Mg brine eventually seeped through extensive beds of calcite, normally dolomite would be formed (along with a calcium chloride brine, or gypsum if the end liquor contained concentrated magnesium sulfate). In the massive marine halite and potash formations dolomite and a high-magnesium/calcium chloride brine are very common results of this reaction, but in lacustrine formations where the ratio of end liquor to calcite may be much larger, magnesite may become the dominant carbonate mineral that is formed.

A slightly different example of magnesite formation in 10 small Spanish playas, with emphasis on Guallar Lake, has been described by Pueyo and Ingles Urpinell (1987). These lakes in the Ebro Basin receive some drainage from the area's massive glauberite deposits, and thus contain sodium sulfate as well as sodium chloride and magnesium sulfate. Calcite is the dominant carbonate in the lake's top 20 cm, but below that in the central portion where strong end liquors can form, dolomite is present, changing at greater depth to magnesite. At 50 cm depth magnesite can represent as much as 50% of the insoluble sediments. In this zone there is also a high CO₂ level from decaying organic matter, causing the authors to conclude that magnesite formed both by the magnesium replacement of calcite, and by direct precipitation with the carbon dioxide. Because of its higher density the stronger-magnesium brines would seek the deeper strata, and thus the reactions would only occur below a certain depth.

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ARGENTINA

Cerro Blanco

The Cerro Blanco deposit of Argentina is a relatively small thenardite (Na_2SO_4) formation located 18 km southeast of Rodeo, and 2.4 km east of Las Flores, Departamento Inglesia, Province of San Juan (Andes foothills, 1100 km WNW of Buenos Aires; Figure 2.1). It occurs in Tertiary sediments of the Upper Member of the Rodeo Formation, a Pliocene sequence of clay, shale, gypsum, and volcanic ash. The thenardite lies in an approximately north–south direction, with a dip of about 15° to the west. There are four “mineralized levels” (beds) containing multiple lenses of thenardite of various dimensions, occasionally interbedded with similar lenses of gypsum that have been transformed from anhydrite. The matrix material surrounding the thenardite is claystone or mudstone, usually with a reddish or yellowish brown color.

The mineralized levels are distinctive in containing two forms of the thenardite lenses (Fig. 2.1). Some levels contain lenses that are several meters long and up to 10 cm thick, with the combined levels’ thickness being 40–50 cm. In other levels the lenses are smaller, generally not more than 10 cm long and 5 cm thick, but much more closely packed, and again in zones 40–50 cm thick. However, these levels have had more sodium sulfate leaching, making the former type contain the higher grade ore. The thenardite is quite pure in both types of lenses, with almost no halite, and a small amount of magnesium and potassium. The area of the deposit is estimated to be 4.2 km^2 , the zones’ average thickness 0.44 m, and the ore grade 24.8–33.7% (weighted average 29.8%) Na_2SO_4 . This indicates estimated reserves of 1.2 million mt of sodium sulfate (Saavedra, 1983).

In an earlier article Kittl (1946) described one of the thenardite outcrops as being interlayered as follows (from the base upward): 3 cm of thenardite, 4 cm of clay, 10 cm thenardite, 12 cm gypsum and clay, 6 cm thenardite, 10 cm gypsum and clay, 1 cm thenardite, 10 cm clay, 15 cm of thenardite and gypsum, and then ferruginous

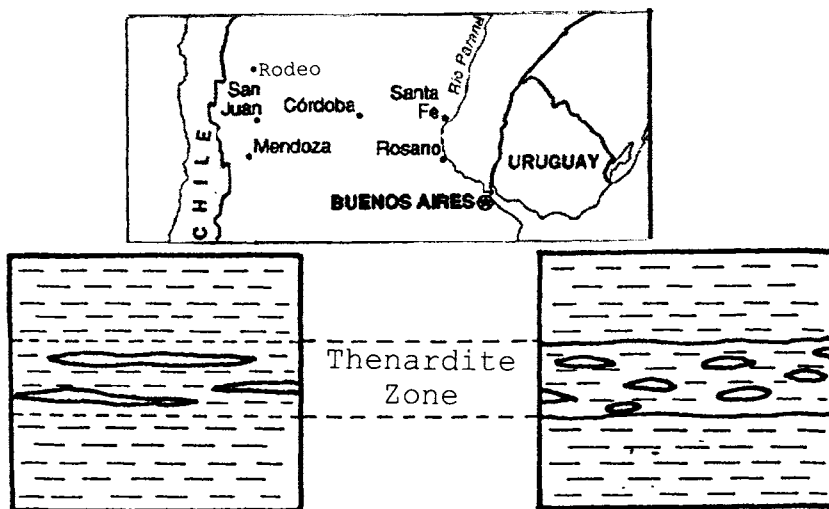


Figure 2.1 Typical shapes of the thenardite lenses at Cerro Blanco, Argentina (from Saavedra, 1983).

clay. The average outcrop was 0.34–0.39 m thick. The thenardite crystals were quite large in the thicker lenses, and smaller in the thinner lenses. The layers of gypsiferous clay that separated the lenses also contained some thenardite.

The crystals inside the beds were colorless, transparent, and with a “weakly vitreous shine,” but at the outcrops had been partly transformed into mirabilite. The thenardite appeared to be very pure, but one analysis showed the following rather unexpected results: Na_2SO_4 91.04%, K_2SO_4 4.60%, CaSO_4 2.46%, MgSO_4 0.73%, NaCl 0.02%, H_2O 0.56%, and insolubles 0.59%. The author felt that the potassium sulfate was in solid solution with the thenardite (he stated that a 10% concentration was possible), but its presence is quite unusual. The large amount of volcanic ash in the deposit may have been the potassium source, and if actually present it would have most likely been in the form of glaserite ($\text{Na}_2\text{SO}_4 \cdot 3\text{K}_2\text{SO}_4$) crystals with the thenardite.

CANADA

Weldon, New Brunswick

There is a large, deeply buried deposit of glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$) in the Weldon-Gautreau Basin just north of Hillsborough in southeastern New Brunswick. It occurs in the upper part of the Lower Carboniferous Albert Formation, overlying at least 60%, and grading into a (13 km^2 [5 mi^2]) halite (NaCl) deposit in the small non-marine Weldon-Gautreau Basin. In three of the six drill holes into the formation

there was an initial 2.4 m (8 ft) glauberite bed averaging 29.6% Na_2SO_4 at an average depth of 344 m (1130 ft). Beneath that at an average depth of 410 m (1350 ft) there was a 10.7 m (35 ft) glauberite bed averaging 26.4% Na_2SO_4 , 8.7% CaSO_4 (anhydrite), and 0.37% NaCl . In one hole under the glauberite there was a sharp change to 140 m of an impure halite zone (47.0% NaCl , 16.8% Na_2SO_4 , and 6.8% CaSO_4). Then the more typical halite began, averaging 180 m of 82.6% NaCl , 5.6% CaSO_4 , and 2.7% Na_2SO_4 . A sample of brine found in the lower section of the main salt body contained (on a dry basis) 96.32% NaCl , 2.07% Na_2SO_4 , 1.44% CaSO_4 , 0.07% $\text{Ca}(\text{HCO}_3)_2$, 0.05% MgSO_4 , and 0.04% R_2O_3 . In some of the other holes, the transition from glauberite to halite was more erratic and spread over a longer distance. The insolubles with the glauberite and halite consisted of calcite and shale. The total glauberite reserves contained an estimated 25 million tons of sodium sulfate.

The Albert Formation was deposited in an elongated, northeast trending, block faulted freshwater basin. Its lower sediments consist primarily of sandstone, conglomerates, and bituminous shale, whereas in the upper section the climate became more arid, and the lake in at least the Weldon-Gautreau Sub-Basin evaporated to higher concentrations. The salts that were deposited form an elliptical-concave lens with a series of gentle anticlines and synclines causing the top to be quite irregular. The glauberite crystals are grayish-white to white and are interlayered and mixed with shale and anhydrite. There is only a minor amount of halite in the glauberite's upper section, but much more as it grades into the underlying halite bed (Webb, 1977; Rowbottom, 1963). The glauberite has also been described as "a thick bed, interlayered with Carboniferous shale and mixed with mud" (Edmunds, 1957). In 1961 the Sifto Salt Co. initiated a diamond drilling program on this "sodium sulfate reservation" at Weldon (Anon., 1961), but the deposit was not commercialized.

Cornhill East

A second glauberite occurrence in the Albert Formation was noted nearby (to the northwest) at Cornhill East. However, it was of a much lower grade, only averaging about 8% Na_2SO_4 in a "brecciated mudstone with a salty matrix" layer at a depth of 786–944 m. Only one hole was drilled, presumably into the flank of a salt dome indicated by a gravity anomaly within the Albert formation, but the dome was not intersected at the bottom-hole depth of 944m (Webb, 1977).

CHILE

Nitrate Deposits

The Chilean nitrate deposits contain a large number of minerals, including the soluble sodium sulfates thenardite (Na_2SO_4 , which predominates), mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$), and astrakanite ($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$). Because of

this, by-product sodium sulfate has been produced periodically from this ore since the 1880s, reaching an announced plant capacity of 160,000 t/yr in 1999. In this unique and puzzling soluble salt formation the nitrate or “caliche” ore occurs in the northern coastal desert region of Chile over a north–south range of 700 km, and an east–west distance of 10–150 km, as an almost continuous deposit (but of quite variable thickness and grade) of sodium nitrate and other soluble salts (Fig. 2.2). It is one of only two substantial deposits of sodium nitrate (the mined ore contains 6–10% NaNO_3) reported anywhere in the world, and also the only deposit containing



Figure 2.2 General area of the nitrate deposits in northern Chile (between the Coastal Range and the Andes). From Crozier (1981); with permission of *Mining Magazine*.

water-soluble iodate (IO_3^- ; 0.04–0.08%), perchlorate (ClO_4^- ; 0.02–0.04%) and chromate (CrO_3^{2-}) ions. The formation contains an estimated 1 billion tons of sodium nitrate, and perhaps 1.3 billion tons of sodium sulfate among its other salts (6–15% Na_2SO_4 , 6–10% NaCl , 0.4–1% K, and 0.3–1% B_4O_7). The quality of the ore varies considerably over the vast deposit, and in its thicker zones is usually most concentrated at a 1–5 m depth.

It has been suggested (Garrett, 1985) that the more common ions in the deposit came from higher elevation salars and thermal springs, as well as the leaching of the adjacent terrain. There is a considerable flow of groundwater from the higher Andes' snow and rain to the lower valleys, primarily through faults and underground aquifers. The entire area has only one river of any size (the Rio Loa), and the extremely arid terrain has almost no features of running water. However, the underground Andes water has resulted in a relatively high water table in many areas, and normal capillary movement has resulted in the slow evaporation of some of this water. This has been assisted by the extremely hygroscopic nature of the nitrates, depositing the salts, and then the very rare rainfall has partially leached the upper surface and mixed the salts in the deposit.

Catalytic nitrogen oxidation (by iron and/or titanium-containing sands as has been thoroughly demonstrated in the laboratory) of air in this high-altitude, clear-sky area appears to have produced the nitrogen dioxide, which eventually was converted to nitrates and helped form the higher oxidation salts. Normally the nitrogen dioxide would have been desorbed (vaporized) soon after it was formed, but in this unusual climate there are daily heavy winter morning fogs, followed by clear skies in the afternoon. The fogs often wet the soil up to 6–10 mm deep, and in so doing would react with any nitric oxide that was present. Some of this solution would seep further into the soil, other portions would be further oxidized near the surface, and some would be desorbed. The net result would be a slow accumulation of nitrates, to be mixed with the capillary evaporating salts and transported by the rain and wind. The heavy wind action in the area is believed to be the device by which the deposit so uniformly and completely spread over all of the terrain in this high-altitude valley between the Andes and the Coastal Range.

CHINA

There are numerous reports of buried ancient deposits of sodium sulfate minerals in China, but few detailed descriptions. Qu Yihua (1989) speaks of "many glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$) deposits being widely distributed in China, but seldom exploited" and being "essentially non-commercial" at present. He described one in the *Xinagouzhuai Formation* in the *Lixian Basin*, Hunan province, as containing 164 m of water-infiltrated "siltstone and mudstone with interbedded glauberite and anhydrite (or gypsum [$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$] layers," and many glauberite beds (up to 42) 1 cm–2 m thick, as well as fractures filled with high-purity mirabilite. Some of the accompanying gypsum occurs as pseudomorphs of glauberite, indicating that the

mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) probably resulted from the leaching of glauberite. Also in the Hunan province, Long and Wang (1994) noted that the *Hengyang Basin's* Lower Tertiary lacustrine sediments contain beds and lenticular masses of glauberite that were analyzed as 25–38% Na_2SO_4 . They are interlayered with shale, impure halite (43–54% NaCl) and gypsum–anhydrite (45–70% CaSO_4). Yang (1989) discussed the origin of the Mesozoic–Cenozoic glauberite deposits in this basin, and also noted that glauberite deposits were common in East China. Many different crystal habits have been observed (Fig. 2.3).

Cretaceous to Tertiary continental deposits of glauberite have also been reported in the *Sichuan Basin* of China. They appear to have been formed by the early diagenesis of sulfate minerals in extremely shallow-water environments, since the glauberite is found in the center of large basins in gypsiferous or gypsiferous-halite sediments (Arakel and Cohen, 1991). Eocene glauberite and other sulfates have also been reported in the *Q Basin*, Hubei province (along with some langbeinite [$\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$]; Xu *et al.*, 1982), and several articles discuss the presence of glauberite beds in a halite (NaCl) deposit in the *Anning Basin* in Yunnan province. Zhu and Hu (1989) state that there is “very abundant glauberite in the salt-bearing system of the Anning Formation.” The glauberite occurs in four forms: bedded, disseminated, interbedded with halite, and in veins. It was felt that the deposits originated by various means: the reaction of an intruding high-calcium groundwater with mirabilite or a high-sodium-sulfate brine, reaction of a high-sodium-sulfate brine with gypsum, or by the leaching and redeposition of other glauberite formations.

A number of other articles discuss mining and processing methods for large, ancient, deep glauberite, thenardite (Mo, 1997), and mirabilite (Sun and Tang, 1996) deposits. This includes well logging (Zeng *et al.*, 1994; Wang and Zhao, 1992),

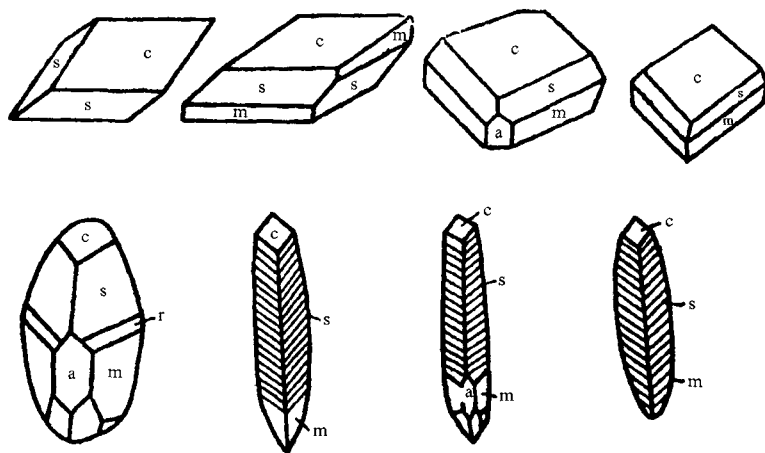


Figure 2.3 Crystal shapes of glauberite in the Anning Basin halite deposit ($c = 001$, $s = 111$, $m = 110$, $a = 100$, $r = 223$). From Yang Qingtang (1989).

open-pit mining, insitue leaching, mud removal from the ore, analytical procedures, and general processing.

The Yikezhao Chemical Industry General Corporation produces much of the natural sodium sulfate in China, with a production in 1997 of 200,000 t/yr of anhydrous sodium sulfate and 95,000 t/yr of sodium sulfide (Na_2S). Some of their production is as a coproduct with sodium carbonate from ancient deposits, or playas with a mixed brine content. An example of the former is the *GiaGanNoer* mine in Suneiteyouqi, Xilingguole league, Inner Mongolia. The overburden for the deposit is less than 20 m thick, and the ore contains 26.6–29.0% trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), 10.0–11.9% sodium sulfate (mainly as burkeite [$2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$], with some thenardite and mirabilite), and 1.2–1.4% halite (see Table 3.6). The sodium sulfate reserves in 1997 were 7 million tons, and 26,000 t/yr of burkeite were produced (Li Wu, 1997).

MEXICO

Bacadehuachi

A large, old (the basement basaltic flows of lava and andesite are of Oligocene or Miocene age) buried deposit of primarily thenardite (Na_2SO_4), with lesser amounts of mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), occurs in the Bacadehuachi Valley of Sonora, 190 km (300 km by road; Rodriguez, 1995) northeast of Hermosillo, and 4 km north-northeast of the town of Bacadehuachi. The thenardite outcrops in the Baucarit Group Formation for 6 km along the valley and appears to have a width of up to 4 km, forming an area of about 13 km². The deposit is in a block-faulted basin that forms part of a tectonic series of staggered blocks that make up the Occidental Sierra Madre Mountains. The generally pure and massive sodium sulfate salts occur in fine-grained vitreous and ashy tufa in a lacustrine section within the upper part of a 600 m thick volcanic–sedimentary sequence. The lenticular beds vary from centimeters to 20 m in thickness, and near the outcrops the thenardite may be covered by 10–30 m of unconsolidated surface rock. Elsewhere it is buried by up to 250 m of volcanic ash and lacustrine sediments (Rodriguez, 1995).

An excavation in one outcrop, the Oro Blanco pit, contained ore averaging 95–99% Na_2SO_4 , and immediately over the deposit was a layer of reddish clay (McIlveen and Cheek, 1994). At other outcrops the deposit appears to be located under a partially dissected alluvial fan that covers it with 0–10 m of conglomerate, and that is cut by gullies to divide the deposit into several isolated sections. The top 2 m of the deposit consists of up to 10 cm thick beds of thenardite with thin clay partings, with the upper ones being more massive and pure. There is some organic matter in the thenardite, and no evidence of gypsum in it or the adjacent clay. The total reserves of the deposit could be nearly 100 million mt of Na_2SO_4 , but this figure is very uncertain (Garrett, 1980).

MINOR DEPOSITS IN EUROPE

Many occurrences or small deposits of sodium sulfate minerals have been reported in various European countries. For instance, in *Belgium* there is sulfate efflorescence on various Carboniferous rocks (Van Tassel, 1973). In *Bulgaria*, thin glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$) beds and isolated crystal clusters of glauberite occur in the halite (NaCl) deposit at Mirovo (Veneva *et al.*, 1967). In *Germany*, some glauberite and thenardite (Na_2SO_4) beds occur in the Wiener gypsum deposits near Lake Grundl, Styria (Kirchner, 1974), glauberite is found in borings near Bunter in the Black Forest (Kaess, 1967), and mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) is found in the halite in the Saarlouis District at Ihn (Mueller, 1969). The Triassic dolomite formation in Perkupa, northern *Hungary*, contains glauberite crystals in association with anhydrite and gypsum in solution cavities (Mauritz and Csajaghy, 1953). In 1923 in *Italy* there were reports that “a well-financed company in Catana” began production of sodium sulfate from mines in the territory of Montedero, province of Girgenti (Wells, 1923). Various soluble sulfate salts (astrakanite ($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$), burkeite ($2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$), glauberite, and thenardite) have also been noted in some volcanic areas of Italy (Garaveli *et al.*, 1997).

In *Poland*, thin glauberite seams and scattered crystal clusters in anhydrite occur in the Permian (Zechstein) Klodawa salt dome (Fijal and Stanczyk, 1969). In Bosnia and Herzegovina, the lacustrine halite deposit of Tuzla contains beds of each of the sulfate minerals thenardite, mirabilite, and glauberite, and much smaller amounts of nahcolite (NaHCO_3), bradleyite ($\text{MgNa}_3\text{CO}_3\text{PO}_4$), and northupite ($\text{MgNa}_2(\text{CO}_3)_2 \cdot \text{NaCl}$). There are five series of halite beds, numbered from 1 to 5 from the top downwards, with most of the sulfates in beds 2, 3a, and 3b. The thenardite occurs in the form of yellow to dark brown platy crystals in association with mirabilite, halite, and some northupite within the 3a and 3b halite series. It is also found in pure beds up to 20 cm thick in the marly shales in the roof of the 3a series. Typical analyses are 54.50% SO_3 , 41.72% Na_2O , 1.34% Cl , 0.96% Na , 0.52% HCO_3 , 0.13% MgO , 0.08% CaO , and 0.75% H_2O , with a density of 2.68 g/cc. Glauberite occurs near the base in the faulted outer edges of the 2 series, next to brecciated water-bearing anhydrite. There are also thin beds in the marly-anhydrite–shale breccia in the floor of the 2 halite series. It is in the form of milky-white crystal aggregates or in elongated fibrous crystals when occurring in fissures. Typical analyses are 50.38% Na_2SO_4 , 49.37% CaSO_4 , and 0.25% SiO_2 , with a density of 2.82 g/cc (Anon., 1982; Janjic and Jovanovic, 1971).

NAMIBIA

Otjiwalunda Playa

The Otjiwalunda playa contains a large concentration of sodium carbonate and sulfate salts as an old, massive, dry, exposed surface deposit, with an estimated 80 million t of equivalent Na_2SO_4 , and 40 million t of Na_2CO_3 . It is located 80 km

west of the large Etosha pan, and about 190 km from the railroad at Outjo. The average annual rainfall in the area is about 437 mm, with 44 days/yr of rain, and an average yearly 60% relative humidity. The maximum summer temperatures are $>32^{\circ}\text{C}$, there is some winter freezing, and the altitude is 900 m.

The largest area of the deposit contains primarily thenardite (zones with $>85\%$ Na_2SO_4) with considerable trona ($\text{Na}_3\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), and lesser amounts of the other minerals. The next largest zone contains fairly equally distributed mixed salts ($\sim 50\%$ Na_2SO_4), and smaller zones contain predominantly burkeite ($2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$) or almost pure trona ($>60\%$ Na_2CO_3). Most of the ore has only 2–3% insolubles, and it all appears to be strip-minable with little or no overburden and a fairly solid black clay underneath. Laboratory tests have also indicated that the minerals in the deposit can be reasonably well separated from each other by simple flotation steps (Garrett, 1992; Foshag, 1933).

Caliche

A second, much less well known deposit of sodium sulfate occurs in ore resembling the Chilean caliche nitrate deposits. The ore is also found in a coastal plain area that experiences heavy winter fogs, perhaps indicating the same air-oxidation, fog capture mechanism for the nitrates as in Chile.

THE FORMER SOVIET UNION

There have been many ancient, buried sodium sulfate deposits reported in the former Soviet Union, but the amount of detail concerning them is scarce, and many of the references are only available as abstracts. The information that is available has been summarized in the following sections.

Akkala

In Akkala, near the Amudarya delta in Uzbekistan, there are Neogene marine areas and adjacent lacustrine sodium sulfate deposits. In the latter formation there are beds or occurrences of thenardite (Na_2SO_4), glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$), mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), and astrakanite ($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$), along with halite (NaCl) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; Rubanov *et al.*, 1980).

Central Asia, Aral Sea Area

Sodium sulfate deposits have been reported in the Meso-Cenozoic terrestrial sediments of central Asia such as at Tien Shan and the Fuzachi Peninsula (see below; Lukyanov, 1981). Also, the *Kichik-Kul (Aral) salt deposit* on the banks of the Kakomeran River in the Dzhungalsk region contained an 85 m thick, average $\sim 50\%$

glauberite lens, of which 42 m were relatively pure, and 12 m contained some beds with a maximum content of 93% glauberite. The impurity was primarily a calcite–clay mixture, with a little NaCl and magnesite. Approximately 15 million mt of equivalent sodium sulfate were estimated to be present, and the formation was overlain by weathered clayey mirabilite (Grokhovskii, 1978).

Caspian Depression

In the southeastern edge of the Caspian Depression of Central Asia, Kazakhstan, at the eastern part of the *Buzachi Peninsula*, conditions were favorable during the Pliocene–Quaternary salt-forming period for the accumulation of mirabilite, astrakanite, and glauberite. Some bischoffite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$), and epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) were also deposited in depressions in the area's shales and marls (Imaneev *et al.*, 1984; Borisov *et al.*, 1981).

Ili River Valley

A buried natural soda ash deposit occurs in the Ili River Valley, composed primarily of burkeite, halite, and thenardite (Stankevich *et al.*, 1984). The aquifers in the area are of the sulfate type. Also, in the alkaline massifs of the *Ilmen* and *Vishnevy* Mountains in the Urals there is extensive thenardite–mirabilite mineralization (Chesnokov *et al.*, 1982).

Kazakhstan

Permian halite in the *Chu-Sarysu* depression contains beds of glauberite, some disseminated glauberite crystals, gypsum, and anhydrite. The glauberite is in the form of large lenticular beds with considerable detrital material, indicating that it was deposited in an inland lake (Ditmar and Tikhomirov, 1967). Other sodium sulfate deposits in Kazakhstan have been described by Bekurov and Mun (1959), Borisov *et al.* (1979), Enikeeva and Strakhov (1985), and Sinyavskiy and Tikhvinskiy (1990).

Kyrgyzstan

The *Shabyr-Kul*, *Sham-Shikal*, and *Chul-Adyr* salt deposits of the Ketmen-Tyubinsk Basin (see Tien Shan) contain an impure thenardite that appears to be amenable to electrostatic beneficiation. It was deposited in Tertiary sandy clays and marls of lacustrine origin, and also contains some mirabilite and astrakanite (Khostova, 1948). The Chul Adyr mine is a fairly large sodium sulfate producer in this area, mining “substantial beds of glauberite,” as well as some mirabilite (Balapanova *et al.*, 1997; Nikolskaya *et al.*, 1997). In northern Kyrgyzstan, mirabilite also occurs extensively

in Tertiary salt deposits, along with some glauberite layers. The mirabilite is considered to be a secondary mineral formed by the leaching of former, more extensive glauberite beds (Shcherbina, 1949).

Nordwick Salt Dome

In the northwestern part of the Siberian Platform mirabilite has been reported in the Middle and Upper Devonian Nordwick salt dome (on the Yurung-Tumus Peninsula). During each period of this marine halite formation a diversity of sedimentary facies developed, including mirabilite. It is speculated that the sodium sulfate was terrigenous in origin and formed in adjacent basins to be later leached and redeposited with the halite. There are three forms of the mirabilite, and it is also found in the dome's cap rock (Matukhin, 1985; Sokolov *et al.*, 1984; Baranov, 1947).

Tien Shan

In the western part of the former Soviet Central Asia, a series of eight lacustrine intermontane basins at Tien Shan contain sodium sulfate deposits in their Miocene, Pliocene, and Holocene formations (Fig. 2.4). The basins range from 40 to 250 km in length, average 10–20 km in width, and are filled with more than 1500 m (up to 5000 m) of clastic and evaporite deposits. In this formation the salt or gypsum-bearing zone normally is several hundred meters thick and lies in the western or central parts of the basins. The salt-bearing strata always starts with clastics, grading

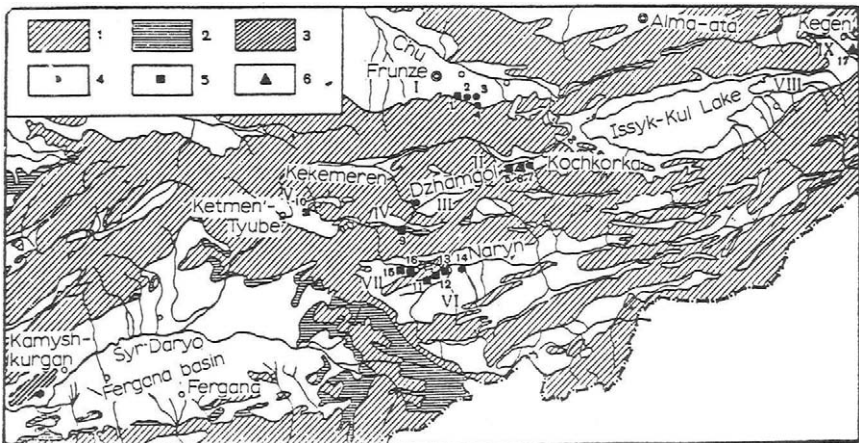


Figure 2.4 The Tien-Shan area of Kyrgyzstan. Legend: 1, Paleozoic; 2, Mesozoic; 3, Samgar-Kamyschkurgan salt region; 4, glauberite; 5, halite and glauberite; 6, thenardite. Intermontaine basins: I, Chu; II, Kochkorka; III, Dzhambul; IV, Kekemeran; V, Ketmen-Tyube; VI, Naryn; VII, Toguztorou; VIII, Issyk-Kul; IX, Kegen. (From Strakhov, 1970; reprinted with the permission of Plenum Publishing.)

into gypsiferous rocks and then soluble salts of two types. In one the sulfates are dominant, with gypsum occurring at the margins of the formation, grading toward the basin center to glauberite, or glauberite with some halite. Pure halite beds are lacking or poorly developed, and halite is a minor component. Thenardite beds may have formed after (above) the glauberite in these basins at *Chu*, *Dzhungol*, *Kochkorka*, and *Naryn*. In the other type of soluble salt deposit halite is the principal mineral (*Fergana*, *Kegen*, *Kekmeren*, and *Toguztorou*; Table 2.1), with gypsum at the margins giving way to pure halite in the center, or halite with a small content of glauberite. There are some beds of thenardite, only a few small layers of glauberite, and in the *Ketmen-Tyube* basin there are occasional beds of astrakanite (Strakhov, 1970).

Among the various Tien Shan basins there are many lenses and beds up to 5 m thick of any or all of glauberite, thenardite, and astrakanite. However, the dominant (98.9% of the total) soluble sulfate in the deposits of the area is glauberite. The glauberite crystal habit is tabular with many twins and intergrowths, and prismatic crystals are rare. Occlusions of 0.11–4.42% of minute gypsum crystals are common, with fewer halite

Table 2.1
Size and Thickness of the Tien Shan Saline Deposits^a

Basin	Length along greatest axis (km)	Width (km)	Thickness of Miocene deposits (m)	Thickness of saline deposits (m)	Remarks
Eastern Chu	—	—	4000–5000	>1000	Lower horizons of salt-bearing series not exposed
Kochkorka	40	>20	>2000	Several hundred m	Because of deformation, the thickness of the saline series was not determined
Dzhungol	70	From 5–10 to 25–30	—	75	—
Kekmeren	60	100	100	Tens of m	—
Ketmen-Tyube	50	10–30	?	260	—
Naryn	250	From 10–15 to 55 on the west	>2000	500	—
Kegen	140	From 10–15 to 40–45	1500–2000	500	—
Ili	—	—	up to 1500	100	—
Toguztorou	—	—	—	—	—

^a Eastern Chu, Kochkorka, Dzhungol, Ketmen-Tyube and Naryn contain sodium sulfates; Kekmeren, Kegen, Ili and Toguztorou halite. From Strakhov, 1970; reprinted with the permission of Plenum Publishing.

and calcite occlusions. Each of the soluble sulfate minerals may also occur as thick coatings, layers, or inclusions in other rocks, and mirabilite is found in the outcrops and weathered zones. The deposits were formed in closed intermountain basins, or chains of subbasins of larger lakes, during successive arid periods (Shcherbina, 1950; Bergman and Shcherbina, 1950). The deposits have several unusual characteristics; for example all of the sediments contain large amounts of clastics. Even the purest gypsum and halite have 1–15% insolubles, and 15–35% is more typical in most of the halite or sulfate deposits. The clay (and most of the other rocks) comprising these clastics is very fine, with normally 75–90% being smaller than 0.01 mm (Popov *et al.*, 1975).

The formation also has an abundance of carbonates: 3–30% in the clay, 1–22% in gypsum, 3–8% in glauberite, and 0.02–10% in halite. Again, most of the carbonate particles are small, generally being 0.005–0.05 mm in diameter. In clay the carbonate is predominately calcite (40–70%), while the gypsum may contain either calcite (CaCO_3) or magnesite (MgCO_3). In the soluble salts magnesite is always the dominant carbonate, dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) is negligible in each of the rock types. No other soluble salts are found in the deposits, although the glauberite always contains 0.001–0.01% strontium (Strakhov, 1970).

The leaching of the soluble sulfate deposits has led to the underground water in the area being high in sodium sulfate, and its springs upon cooling have formed scattered mirabilite deposits up to 7.5 m thick over an area of 78,000 km² (30,000 mi²). These deposits can be either permanent or vary with the season (Dzens-Litovskii, 1962).

Uzun-Su

In the Turkmenian Uzun-Su salt deposit in Central Asia there are layers and lenses of astrakanite, with lesser amounts of thenardite and mirabilite. They occur in the lower part of the Akchagylian basin, often accompanied by sandy clays that are frequently gypsiferous and sometimes faintly calcareous. The astrakanite is colorless, transparent, dull on the surface, and it has a vitreous luster on fresh fractures (Boldyreva, 1937). Reineke (1930) has also discussed these sodium sulfate deposits.

Vishnev Mountains

In the Ural region of these mountains thenardite and mirabilite beds have been reported in the miaskites (miascite), in deep horizons of the alkaline massifs. Some glauberite is also present, along with shortite ($2\text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3$; Chesnokov *et al.*, 1984).

Minor Deposits

In *Kazakhstan* sodium sulfate deposits have been noted that could “be mined for subsequent use in the chemical industry.” The *Kiuren-Dag Mountains* of western Turkmenistan have both thenardite with mirabilite, and thenardite with halite

deposits (Iskyul, 1930). In the *Slepaya* mine there are veins and lenses of thenardite transversing nepheline syenites that have been formed by hypogene processes. Thenardite and mirabilite veins and crusts have been found in the southern slopes of the Crimean Mountains (Suprichov and Albov, 1966).

Glauberite has been reported in many formations, and particularly in salt deposits. It occurs in the Tertiary halite and thenardite deposits of *Kochkorsk* in substantial beds. The *Alabug-Naryn* deposit consists of alternating beds of clayey salt and glauberite, with the glauberite predominating. The deposit is 40 km long, and individual glauberite units can be up to 12 m thick. In the Upper Miocene *Kamysh-Kurgansk* 10–100 m thick salt deposit, there are layers of both clayey glauberite and halite–glauberite, where the glauberite content can reach 10–15%. In the Permian *Lesser Karatau* and *Assa River* deposits there are beds of glauberite in terrigenous sediments at a 600–800 m depth (Strakhov, 1970). Finally, in the Jurassic *Shedoksk* and *Guardaksk* salt deposits (of the northern Caucasus and eastern Turkmenistan, respectively), glauberite is also present as massive beds (Grokhovskii, 1978). General articles on sodium sulfate deposits include those by Bokii and Gorogotskaya (1970), Dzents-Litovskii (1956), Hemy (1969), Ivanov (1967), Levine (1988), Sinyavskii and Tikhvinskii (1989), Teterina (1995), and Visyagin (1951).

SPAIN

Spain appears to have the largest glauberite–thenardite deposits in the world, except perhaps for the less well known Tien Shan (Kyrgyzstan) deposits. Spain's deposits contain an estimated 2.5 billion mt of equivalent sodium sulfate, of which the Ministry of Industry and Energy states that the recoverable reserves are 272 million mt. The majority of these reserves are in two separate basins containing buried deposits, with mining areas in 1999 in the Madrid Basin at Villarrubia de Santiago (Toledo province) by FMC Foret, and at Villacanejos by Sulquisa. The Consuelo (San Martin de la Vega), Vicente (Ciempozuelos), and Comfort mines were closed. In the Ebro Basin there was production at Cerezo de Rio Tiron by Crimidesa, and at Belorado by Minera de Santa Marta (MSM). In this basin there had previously been production at Alcanadre and Ermita de Aradon (Ordenez and Garcia del Cura, 1994, 1992). The Calatayud Basin also contains very large deposits that are less well studied, and not as yet commercialized.

Madrid Basin (Tajo Basin)

Structure

Glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$) and thenardite (Na_2SO_4) have been found in various locations and bed thicknesses (perhaps in a series of subbasins) throughout the 10,000 km² Madrid Basin (Fig. 2.5). The major salt in the deposits is glauberite,

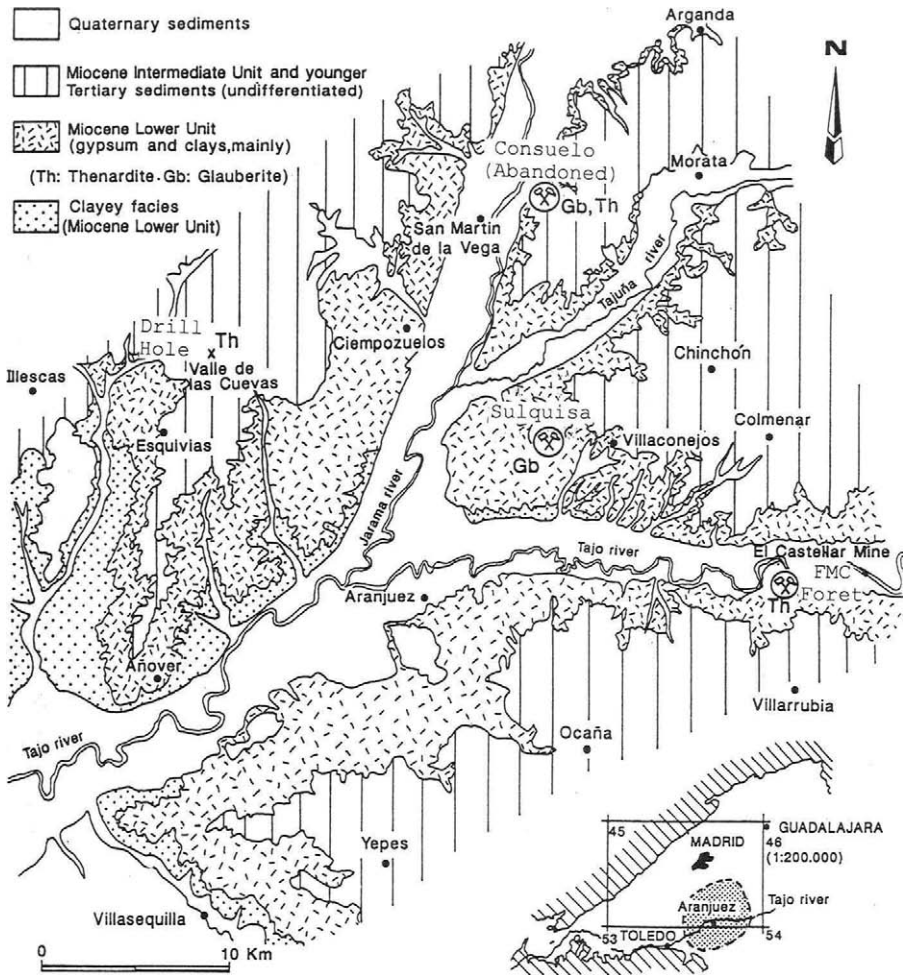


Figure 2.5 Map showing the location of the sodium sulfate mining operations in the Madrid Basin, Spain. (From Orti and Salvany, 1990; courtesy of Dr. Orti.)

with less thenardite, and small amounts of halite (NaCl), polyhalite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and (rarely) astrakanite ($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$). The deposits occur in a Tertiary lacustrine sequence that can be up to 3500 m thick. The lowest <250 m is called the Miocene "Lower, or Saline Unit" and contains mainly evaporites, including the soluble sulfates interbedded with or in a matrix of shale, clay, anhydrite (CaSO_4) or gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and magnesite (MgCO_3 ; Ordonez *et al.*, 1984; Garcia del Cura, 1979). The soluble sodium sulfate zones grades laterally to gypsum, then reddish-green mudstones with anhydrite and/or gypsum

nodules (Ordóñez and López Aguayo, 1982), and finally to coarser clastics (Ordóñez and García del Cura, 1992; Ordóñez *et al.*, 1991; Orti *et al.*, 1979).

The top of the Saline Unit is at an elevation of about 650 m above sea level, and when the glauberite or thenardite is near the surface there is usually up to 50 m (even 60 m) of a leached zone in its upper section where the anhydrite has been converted to gypsum (and in some areas to calcite), and the soluble sulfates dissolved. The gypsum is commonly coarsely crystallized, with some selenites ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and pseudomorphs of anhydrite and glauberite. It can also have numerous solid-phase inclusions, be fibrous, and occur as a vein-filling material. Below that, in the thenardite area to the south of the basin there is up to a 15 m zone where the dominant mineral is massive and fairly pure thenardite. Below the thenardite is a thin bed of glauberite. Further to the north there are scattered locations with both thenardite and glauberite, and then in the remainder of the basin there is a 0–50 m zone where the only soluble sulfate is fairly pure glauberite. At the base of both the thenardite–thin glauberite and the glauberite beds there is a structure that is more uniform throughout the basin: a layer of halite, and under that red clay and halite with some polyhalite and glauberite. Small amounts of these minerals also occur in the underlying shale matrix. Throughout this Saline Unit there are alternating layers about 3.2 mm thick of anhydrite–magnesite–clay (with some quartz [SiO_2], feldspar [Na , KAlSi_3O_8], etc.) with 3–4 mm beds of anhydrite. These rhythmic pairs also occur, but to a lesser extent in the glauberite and thenardite zones (García del Cura *et al.*, 1992, 1986, 1979, 1978; Ordóñez *et al.*, 1982).

Most of the glauberite and/or thenardite deposits have been found in a triangular area with its vertex in the city of Madrid, one side extending to the south, from there north-northeast, roughly perpendicular to the area's central valleys, and then to the northwest back to Madrid. It appears that there were subbasins within this area that formed the individual deposits, since they are generally similar, but the soluble sodium sulfate zone in each has its own specific thickness, purity, and sequence of minerals. The lower section of the deposits, as previously noted, however, is more uniform (Orti, 1999), and the assemblage of minerals indicates that the evaporating conditions and/or the brine's mineral constituents were somewhat different than later in the period when glauberite or thenardite deposited (Ordóñez and García del Cura, 1992).

Thenardite

Thenardite has only been reported at scattered locations in the southern part of the basin (called the Aranjuez area; Fig. 2.5). In this zone it can be seen outcropping in the middle of a cliff along the south side of the Tajo River, and it is easily noted by its white color for a distance of up to 2 km. The outcrops are intermittent and up to 19 m thick. It also outcrops (with some glauberite) between gypsiferous marls near San Martín de la Vega, along the Jarama Valley, and at Ciempozuelos in Madrid province. Thenardite is the dominant mineral in the unaltered rock behind these outcrop lines, but it can be interbedded with abundant glauberite (Rios, 1968).

It has also been noted in a drill core at Valle de las Cuevas (Orti and Salvany, 1991), at Salinas de Espartinas, with glauberite at Chinchon and Colmenar de Oreja, and with mirabilite at Villamanrique (Ordonez *et al.*, 1977).

The thenardite most frequently occurs as massive beds containing aggregates of large (up to 10 cm long) blue anhedral crystals, and to a lesser extent as smaller crystals (including being disseminated in the shale–anhydrite–magnesite matrix) or as a cementing agent (Ordonez *et al.*, 1991). In old fractures thenardite is light gray or bluish, but it is semitransparent in recent fractures. The beds of pure thenardite sometimes have groups of parallel crystals (as the structure of a comb) with one end embedded in large anhedral crystals of thenardite. When it cements glauberite it frequently concentrates on the borders of the crystal masses (they have “reactive rims”), and when the cement contains magnesite, the magnesite also tends to concentrate on the glauberite crystals’ borders. Mixtures of thenardite and glauberite crystals are common, and some appear to have had the thenardite adapt to the form and cavities of the glauberite (Garcia del Cura *et al.*, 1979). In other areas it appears that the glauberite grew from the thenardite crystals (Ordonez *et al.*, 1991). Ordonez and Garcia del Cura (1994) state that the thenardite crystals may have up to centimeter-sized inclusions of other solids, including glauberite, and are usually euhedral in geodes and as a vein-filling material.

In places the thenardite is over an “irregular bed of glauberite decimeters thick,” called “Piedra Negra or Roca Negra (black rock),” and in rare instances (further to the north) there are up to 30 m of glauberite beneath thin thenardite beds. The black rock occurs as “irregular beds of microcrystalline glauberite, with the crystals having wavy rims and many inclusions of magnesite, quartz and mica.” Under the glauberite is a “conspicuous layer of red clay,” and below that a 15 m halite bed (Ordonez *et al.*, 1991). Below the halite there is a 5m bed of somewhat mixed interlayers of halite, glauberite and shale, and beneath that more red clay. Orti *et al.* (1979) provided a detailed stratigraphic analysis of these underlying beds, which are found throughout the basin (Fig. 2.6). Ordonez and Garcia del Cura (1994) described the lower red clay bed as being “reddish saline muds containing crystals of halite, platy lensoid and coarsely crystalline euhedral discoid glauberite.”

Glauberite

Glauberite is by far the dominant soluble sulfate mineral in the Madrid Basin and commonly occurs as massive beds that often contain 3–15 mm thick layers of dense aggregates of euhedral, lens-shaped crystals, interbedded with millimeter-thick layers of anhydrite and/or magnesite (Fig. 2.7). The glauberite layers may also be centimeters to decimeters thick, and in both cases they are usually free of occlusions. The long axis of their crystals is parallel to the bedding plain. Glauberite can also occur as fibers and nodules, or as a cement for anhydrite, magnesite, and even glauberite. When the cement is on glauberite crystals it forms a skeletal character that weakly reflects the structure of the initial euhedral crystals, and glauberite pseudomorphs of halite may be present. The contact between beds of glauberite and

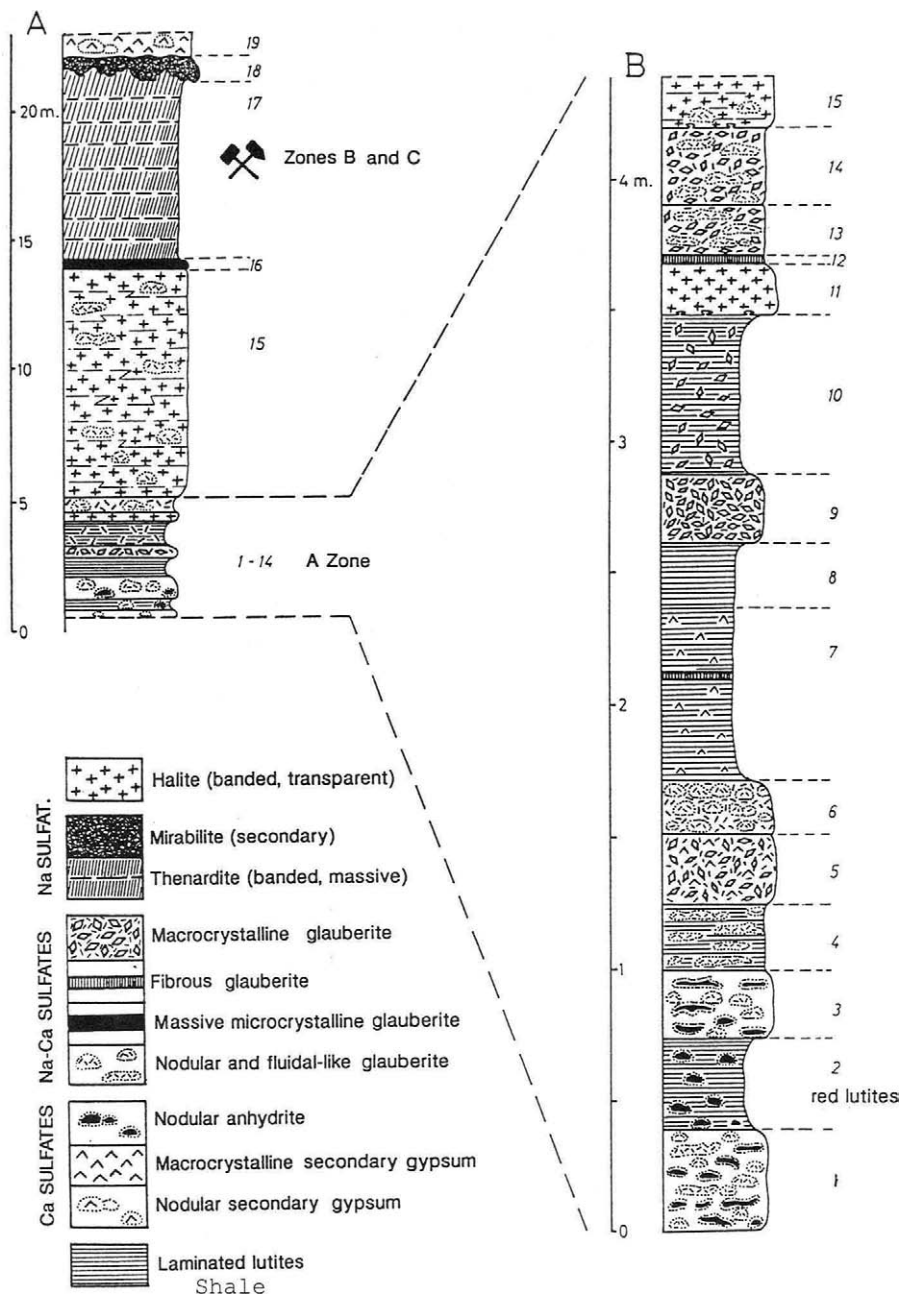


Figure 2.6 Stratigraphy of the soluble sulfate and underlying beds at the FMC Foret mine. (Numbers represent differing mineral or textural layers). From Orti and Salvany, 1990; courtesy of Dr. Orti.

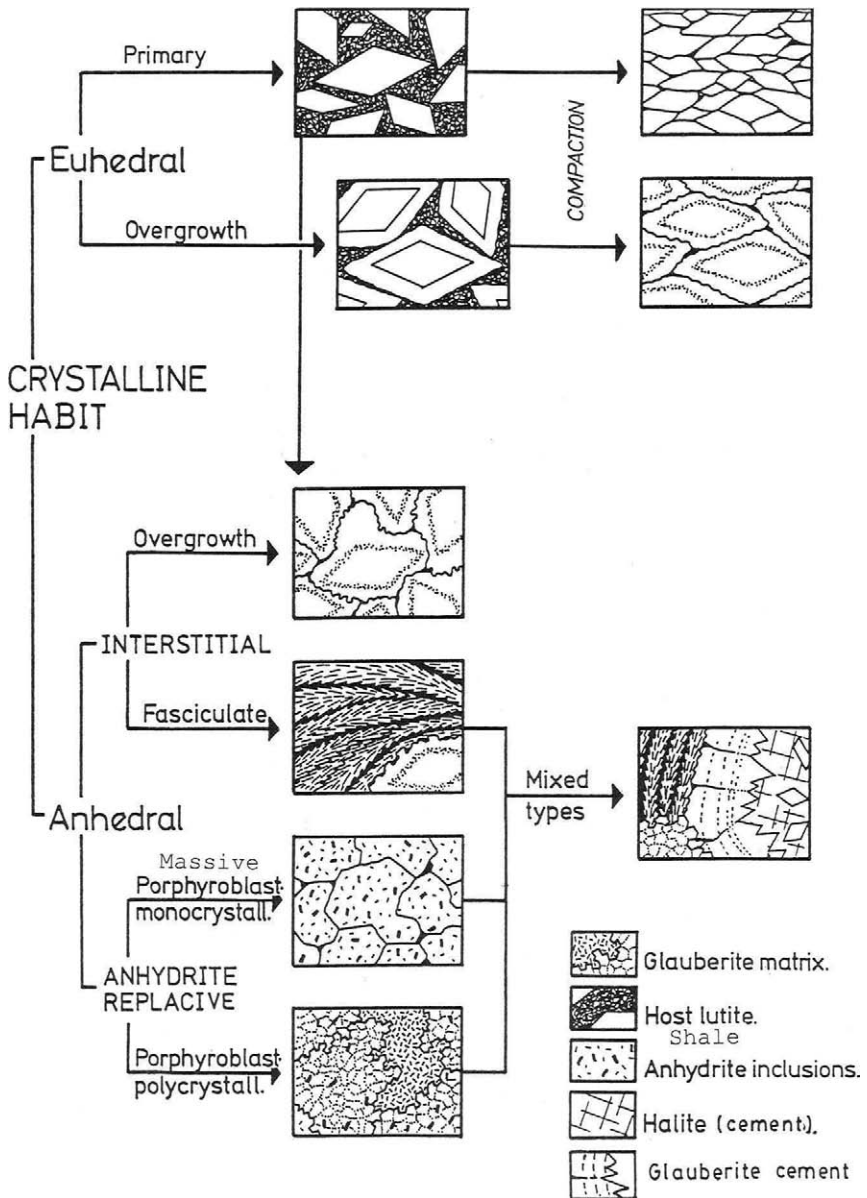


Figure 2.7 Glauberite crystal structure or texture in the Madrid Basin. (From Orti and Salvany, 1990; courtesy of Dr. Orti.)

anhydrite–carbonates (or even mud layers) often appears to have the glauberite somewhat deforming the other beds, as if the glauberite crystals grew into them, or intruded because of the pressure of burial (Garcia del Cura *et al.*, 1979; Ordóñez *et al.*, 1977). Ordóñez and Garcia del Cura (1994) described the glauberite more simply as having “a wide variety of textures and habits,” occurring as massive beds or interbedded with magnesite or magnesite marls, with disseminated crystals or laminae being common at greater depths.

Other Minerals

Anhydrite is present throughout the Saline Unit, generally as thin laminar beds alternating with anhydrite–magnesite (or other minerals), but also as enterolithic “nodules” (intestine-like elongated clusters) of various sizes and shapes. It is usually found as euhedral tabular crystals, but many odd forms are also present, such as platy or “bow tie” in the deepest zones. *Halite* usually occurs as thin (a few centimeters thick) continuous beds interlayered with other thin beds. The crystal faces may be parallel to the substrate or have upward-facing chevron structures, and the crystals usually have abundant fluid and/or solid inclusions. However, halite can also be present as a cement for other rocks, and as isolated single crystals throughout the formation, including in high-grade glauberite (even as occlusions in it), but rarely in thenardite. *Magnesite* always has a micron-sized ($<2\ \mu\text{m}$) texture, making even microscopic identification difficult. It is the principal carbonate mineral in the Saline Unit, occurring as continuous thin beds or as an intercrystalline material (Garcia del Cura and Ordóñez, 1992).

Polyhalite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is found in small quantities in the Saline Unit, invariably in the halite and clay structures beneath the glauberite, and often at elevations below about 520 m (Fig. 2.6). It usually has a spherical habit or consists of crossed microfibrils, and occurs as thin (millimeter-sized) green layers with minor magnesite, alternating with magnesite containing minor polyhalite, as inclusions in halite, or felty masses on the margins of glauberite crystals (Ordóñez and Garcia del Cura, 1994, 1992). Orti and Pueyo Mur (1980) note that it is found in 1–10 cm thick beds containing mostly halite, but also with some glauberite, gypsum, and anhydrite. There are many polyhalite pseudomorphs after gypsum, glauberite, and perhaps mirabilite, indicating that it originated from the reaction of these minerals with a strong Mg and K brine that was probably an end liquor from the evaporating lake or playa. With currently evaporating brines this composition would be reached at the end of the halite, sodium sulfate, and/or potash depositing periods.

Mining Operations

FMC Foret

More detail on the thenardite beds can be obtained in the *El Castellar* mine, operated by FMC Foret in the municipality of Villarrubia de Santiago, Toledo province. Its general stratigraphic column is as follows (from the base up; Fig. 2.6): 5 m of

reddish shale with layers of halite that may contain some glauberite and/or nodular anhydrite and quartz ("red clay"); 3–5 m of halite–glauberite–shale; 8–15 m of halite with varying amounts of anhydrite; an average of 5–10 m of thenardite that usually contains some glauberite and/or insolubles (this is the bed being mined; "7 m, with scant euhedral crystals of glauberite" Ordonez *et al.*, 1991; "up to 8 m with ~10% glauberite" Ordonez and Garcia del Cura, 1994); 0.2–0.6 m of mirabilite; and finally, the overlying gypsum that was usually massive and in a selenite, crystalline, or nodular form (Orti *et al.*, 1979). At the outer edges of the thenardite there is a modest section of glauberite. The composition of the clay in the matrix, the interbeds, or the underlying shale includes 80% illite, 15% kaolinite, and 5% chlorite. The insolubles with the thenardite are primarily gypsum, magnesite, and clay. The thenardite in 1971 was at an elevation of 520–535 m, with an average equivalent Na_2SO_4 content of 62.5% (Ordonez *et al.*, 1982).

Rovira (1960) described the thenardite bed being mined at that time as 5–6 m thick, horizontal, containing only a small amount of glauberite but resting on a thin glauberite layer, with a clay marl and halite underneath. The deposit had an area of 30 km², and the reserves were 200 million mt of Na_2SO_4 . The bed had areas of discontinuity caused by water intrusion and leaching, which were later filled by clay and marl. The thenardite occurred in two physical varieties, one blue and the other white, with the blue being harder. The white variety also had two types: one compact, and the other somewhat disintegrated, as if by the action of water. There was also some mirabilite at the top of the formation, occurring as a compact mass or in granular groupings. The glauberite in or below the thenardite also had two forms, with one yellow, crystalline, and occurring in clay layers or sometimes inside masses of blue thenardite. The other form was black, compact, and in clearly differentiated layers. The average chemical analysis of the ore in 1960 was 70–75% Na_2SO_4 , 11–17% CaSO_4 , 0.4–0.6% NaCl , 3–9% insolubles, and 1–5% water.

The Piedras Negra glauberite (under the thenardite) consisted of large anhedral crystals, sometimes interlayered or mixed with anhydrite, magnesite, and some quartz and mica. Orti *et al.* (1979) noted that most of the glauberite in the thenardite was in a massive microcrystalline form, and that there were some thin interlayers of hydroglauberite ($5\text{Na}_2\text{SO}_4 \cdot 3\text{CaSO}_4 \cdot 6\text{H}_2\text{O}$) consisting of small white fragile crystals. The glauberite contained many inclusions of quartz and magnesite, had "diffuse and sinuous contours," and "cloudy structures formed by small crystals of similar orientation" (Garcia del Cura *et al.*, 1979).

Sulquisa

The Sulquisa deposit provides similar details about the thicker, higher-grade glauberite deposits. It is located in the province of Madrid, north of the Tajo River, west of Cienpozuelos, and near a highway 5 km south of Titulcia toward Villacanejos. The Saline Unit there is at an altitude of 600 m, and the approximately 20 m of overburden in the mining area has been thoroughly leached. This has left cavities, layers of gypsum with selenites, and abundant mirabilite efflorescence. Under the altered zone is a 25–45 m bed of high grade glauberite (Fig. 4.23) containing some

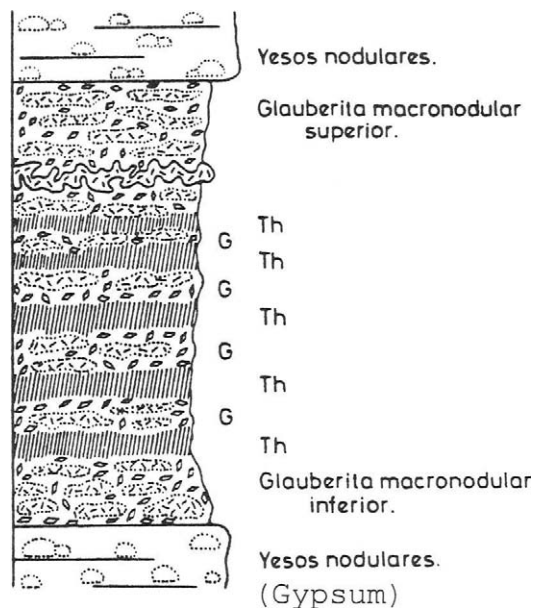


Figure 2.8 Glauberite–thenardite ore at the Consuelo mine. (From Orti *et al.*, 1979; reprinted by permission of the editors of *Boletín Geológico y Minero*.)

centimeter-thick interlayers of crystalline magnesite and magnesian shale. There are also variable amounts of anhydrite with the glauberite, and some halite and astrakanite, but very little thenardite and mirabilite. The ore is basically quite pure, averaging 40–42% Na_2SO_4 . Below it, at an elevation of 500 m, the presence of halite in the shale increases, and below the 450 m level there are significant amounts of polyhalite (Ordonez and Garcia del Cura, 1992; Coope, 1983).

Other Mines

Among the former mines near the Tajo River, the Comfort mine at Ciempozuelos has not been operated since 1936, and it was reported to have worked with rooms and entries that had a considerable roof span. Their glauberite was partially gypsiferous and contained some thenardite and astrakanite (Ordonez and Garcia del Cura, 1992). The Consuelo mine at San Martin de la Vega worked a 6 m thenardite–glauberite bed (Fig. 2.8) that was roughly at the same level as the thenardite in the El Castellar (FMC Foret) mine 25 km to the southeast. Operation at the Vicente mine in Villacanejos terminated in 1968, having produced only 50 t of a 97% purity sodium sulfate for the detergent industry. The glauberite bed that they mined had a thickness of 10–12 m (Fig. 2.9). At *Carcaballana* (Villamanrique de Tajo) and *Espartinas* (Ciempozuelos) small amounts of sodium sulfate have also been produced by leaching ore, and then allowing mirabilite to form from this brine in ponds during the winter (Ordonez *et al.*, 1982).

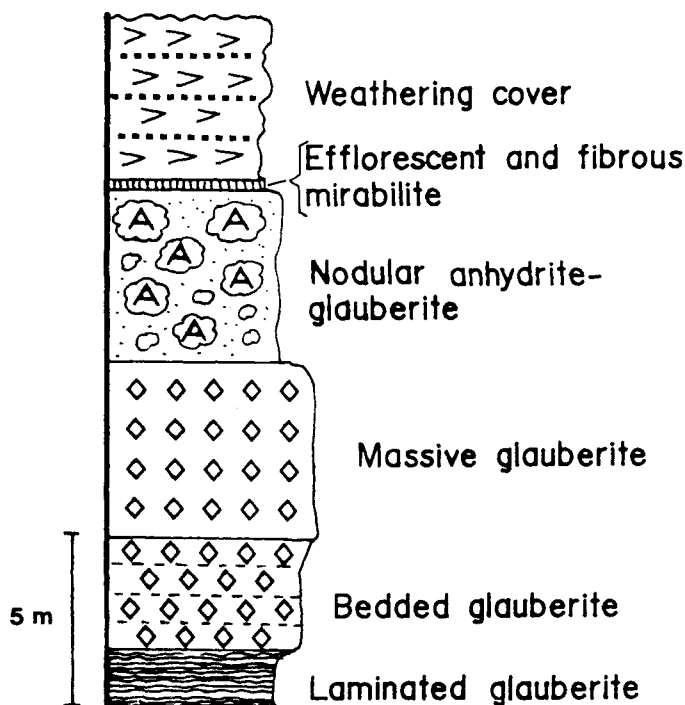


Figure 2.9 Stratigraphy of the ore in the Vicente mine. (From Ordóñez and García del Cura, 1994; reprinted by permission of the Society for Sedimentary Geology.)

Ebro Basin

This large elongated and contorted depression in northeastern Spain (Fig. 2.10) has an area of approximately 50,000 km². It is bounded by the Pyrenees Mountains to the north, the Iberian Ridge (Massif) to the southwest, and the Catalan Coastal Ranges (Cordillera Costero-Catalan Mountains) in the southeast. The basin's lacustrine fill is Tertiary, and its most important sediments range in age from early Oligocene to late Miocene. The sediments in the basin are up to 3 km thick, with zones that are predominately gypsum interlayered with fine-grained siltstones and mudstones. The basin has three major subbasins containing glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$): Rio Tiron-Belorado, Alcanadre-Arrubal, and Remolinos-Zaragoza (Salvany and Orti, 1994). It appears as though they formed in one large basin that had its depocenter shift from the east to the west to form the glauberite deposits, since each deposit is of a different age. However, they also vary chemically, having considerable halite and some thenardite with the glauberite at Zaragoza (the eastern and oldest area), and the glauberite being very pure with only a small amount of halite in the underlying clay at Rio Tiron-Belorado (the western and youngest

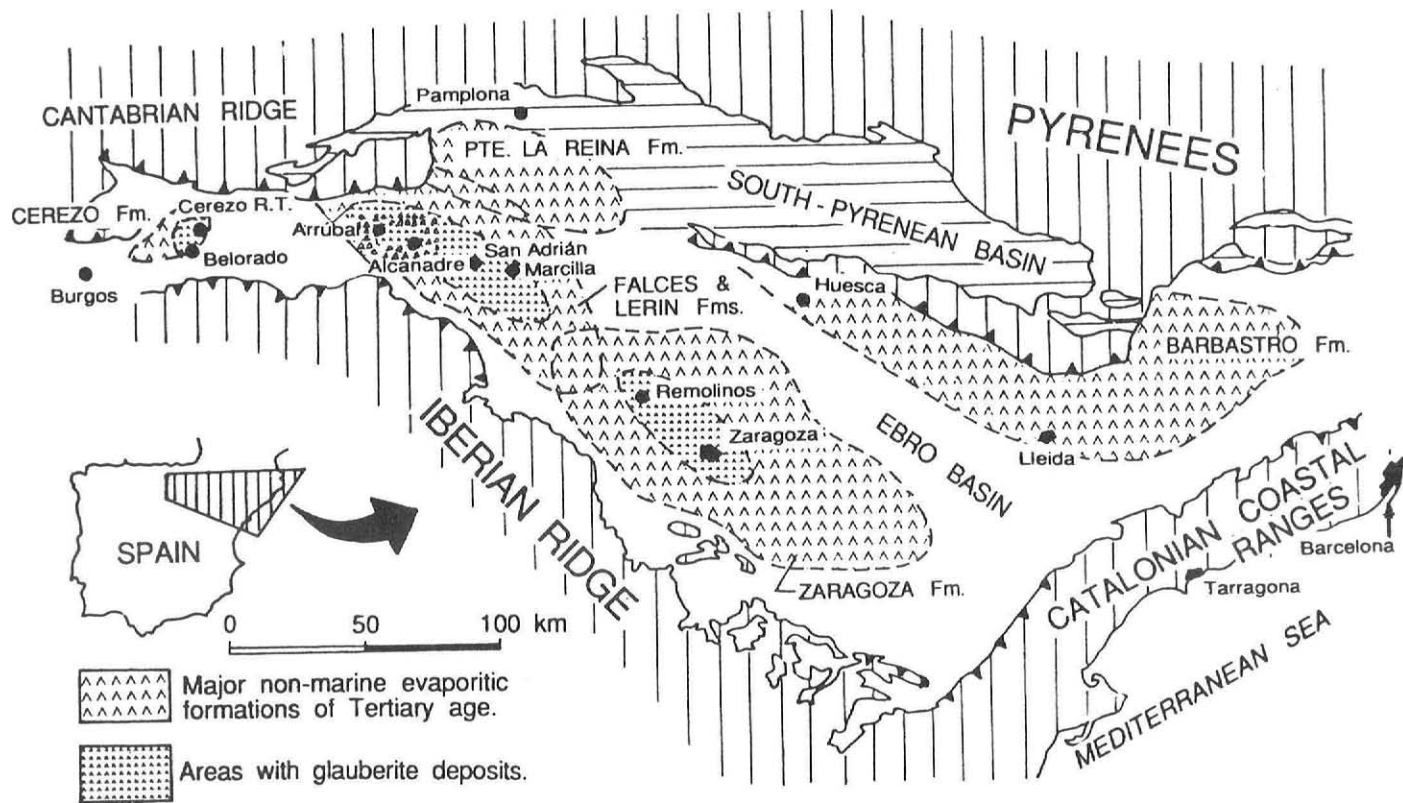


Figure 2.10 Geologic map of the Ebro Basin. (From Salvany and Orti, 1994; reprinted by permission of the Society for Sedimentary Geology.)

deposit). As with the Madrid Basin, the Ebro Basin is surrounded by mountains containing marine formations with some gypsum and clays, and both are near other closely related basins that do not contain glauberite (Orti, 1999). In the far eastern section of the basin, the Los Monegros area, there is considerable alkaline soil and numerous playas containing some thenardite/mirabilite, astrakanite, or polyhalite.

Rio Tiron–Belorado Area

The glauberite beds in the *Rio Tiron* area of Burgos province's Ebro Basin are located in the predominantly gypsum Cerezo Formation. The glauberite usually contains some gypsum/anhydrite and a dolomitic marl (Fig. 2.11) and alternates with

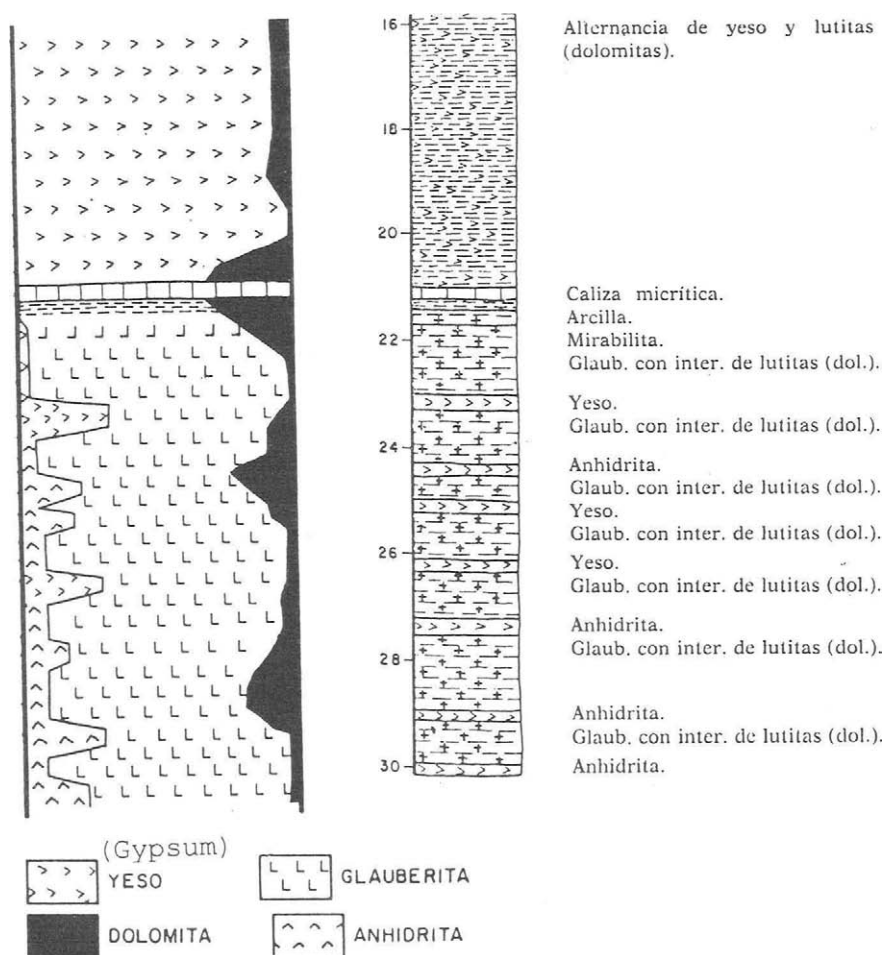


Figure 2.11 Typical composition of glauberite at Rio Tiron. (From Menguina *et al.*, 1984; reprinted by permission of the editors of *Boletín Geológico y Minero*.)

beds of variable thickness of these materials. The clay in the marl consists of predominantly kaolin and detritus of mica, quartz, and feldspar. In a few zones there are adjacent sandy beds made up of quartz-feldspar (in a ratio of ~3:1) and a carbonate-gypsum binder in variable proportions. When the sulfate formation is near the surface, the anhydrite down to the water table has been converted to gypsum, and the soluble sulfates dissolved. Immediately under the leached zone there may be a layer that contains thinner or lower grade glauberite with abundant mirabilite efflorescence that is not commercial. Some of the anhydrite in the glauberite has also been converted to gypsum (Menduina *et al.*, 1984; Ordonez *et al.*, 1983).

Near the town of Cerezo de Rio Tiron in the northeast area of the Rio Tiron-Belorado deposit, four beds of glauberite outcrop for 1 km along the steep Miocene lacustrine marl banks of the Tiron River. Their average thickness, from the top down, is 2 (A bed; the upper O bed is not always present), 8, 4, and 2 m, although a combined glauberite thickness of up to 20 m is not unusual. The upper (A) and second (B) beds are separated by 4–6 m of marl (also called “clayish shale and gypsum”), the second and third by 1–30 m of marls and gypsum (clayish shale and anhydrite), and the third and fourth (D) by 1–10 m of the same material. Some of the ore can be characterized as consisting of couplets of glauberite beds containing some dolomite with layers of anhydrite-dolomite. The 8 m thick B glauberite bed was being mined in 1984 and had a 60 cm anhydrite bed in its midsection. The glauberite was compact and medium-grained, the bed was almost horizontal and fault-free, and it averaged about 40% Na₂SO₄. In the overburden there was micritic calcite with algal films, thin layers of calcified glauberite crystals, and many glauberite pseudomorphs after gypsum (Menduina *et al.*, 1984; Ordonez *et al.*, 1982; Rios, 1968).

In a nearby bore hole there were six beds of glauberite (including the upper Grupo Belorado and O beds; from the top down, 6, 3, 6, 8, 8, and 8 m thick), with each containing layers of glauberite alternating with larger or smaller layers of anhydrite, dolomite, and/or marl. The marl often was the dominant host rock, although it also could be present only as an intercrystalline material, especially where the glauberite was more pure and massive. The anhydrite was not always present as continuous layers, but frequently occurred as nodules of millimeter to decimeter size. Between the glauberite beds there were some beige-colored calcareous layers (16–20 cm thick), with alterations of micron-sized fossilifera and sand (used as a marker bed), and under that a clay layer with vegetative fossils. The clays in the deposit were mainly illite with some kaolinite and talc (Menduina *et al.*, 1984).

In a few areas the glauberite occurs primarily as large crystals, densely packed, and with well-developed surfaces even when the crystals are small or have a dolomite cement. The upper edges of the glauberite beds often have a crownlike texture, and microcrystalline anhydrite is occasionally present (Ordonez *et al.*, 1982). Menduina *et al.* (1984) summarized that the glauberite occurred in three forms: massive, interbedded with dolomite, and dispersed crystals in a matrix of carbonates. The massive glauberite is often formed by 0.3–4 mm euhedral or anhedral crystals that may appear to be segregated by size, and/or have 0.06–0.09 mm inclusions of anhedral

anhydrite. The glauberite may also occur as a cementing agent, often on marginal rims to form clusters of cemented crystals.

The amount of insolubles in the glauberite is quite variable, but when it is appreciable, the glauberite is laminated with interbeds of dolomite or sometimes marl. The lamina may also contain some chalcedony (SiO_2), authigenic quartz, or nodules of anhydrite that penetrate into glauberite crystals. When chalcedony is present there may also be pseudomorphs of gypsum after glauberite. In the "mixed-with-dolomite" glauberite the dolomite layers blend gradually into the glauberite. The dolomite also tends to be more microcrystalline and may even have ostracod inclusions (as can be seen in some mine tunnels). The "dispersed" type of glauberite has millimeter-sized glauberite crystals disseminated in a carbonate matrix. In the leach zone there may be gypsum pseudomorphs of these very small crystals.

The ore in the *Belorado* area (at Minera de Santa Marta, or MSM) is similar to that previously described at Rio Tiron, about 30 km to the north. There are also four major beds of glauberite (six counting subdivisions of beds C and D, although in areas where the hills have been less eroded, three or four upper beds also exist). An estimate of the thickness (in meters) of the sum of the "pure" glauberite beds (numbers in parentheses) in each glauberite zone (first numbers), and the barren rock under the glauberite zone (last number), have been averaged from three or four drill holes. In the Cerezo Formation, from the top down, they are as follows: The A bed is 4.0 m thick (containing a total of 2.4 m of pure beds), with 4.4 m of barren rock underneath the A zone; B bed 8.2 (5.5), 2.5; C1 5.9 (5.2), 4.0; C2 (but not continuous throughout the basin) 4.5 (4.3), 2.5; D1 11.1 (9.2), 2.0; and the D2 bed (missing in one hole) 5.9 (5.9). The beds above the Cerezo Formation (based upon one or two holes) are, from the top down, as follows: Unnamed 4.5 (3.8), 13.5; Grupo Rierta 8.3 (3.8), 6.8; Grupo Belorado 15.9 (9.9), 2.3; O bed 4.7 (3.9), and 6.5 m of barren rock to the A bed. The ore contains almost no other soluble salts, and halite is only present in small amounts primarily in the clay underlying some of the glauberite beds (Antonio Cejalvo, 1999).

Alcanadre-Arrubal Basin

In this subbasin the lacustrine sediments could be up to 4 km thick and have been classified into three stratigraphic units. The middle Falces Gypsum Formation (Middle to Upper Oligocene) is 800–1000 m thick, and the upper Lerin Gypsum Formation (Oligocene to Lower Miocene) is 400–600 m thick, with its evaporite portion being 100–200 m thick and 50 km long. The combined Falces and Lerin formations cover an area that is about 100 km long by 30–40 km wide, and both contain glauberite beds. The upper two cycles of the Lerin Formation are called the Los Arcos Gypsum and contain most of the glauberite. There were two major glauberite beds, 2 and 4 m thick, outcropping near the former *Alcanadre-Arrubal mine* (near Logrono), and in some adjacent bore holes thicker and more abundant glauberite layers were found (Fig. 2.12; Salvany and Orti, 1994, 1987). Outcrops of glauberite appear to be continuous upstream along the Ebro River (Birnbbaum and Coleman, 1979).

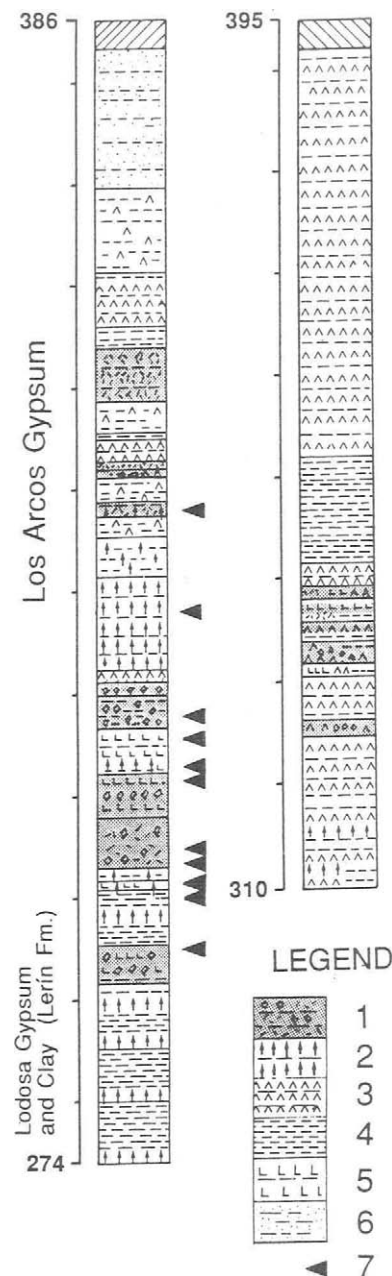


Figure 2.12 Stratigraphy in the Alcanadre–Arrubal glauberite zone. 1, glauberite; 2, anhydrite; 3, secondary gypsum; 4, clay; 5, halite; 6, siltstone and sandstone; 7, interbeds of polyhalite. (From Salvany and Orti, 1994; reprinted by permission of the Society for Sedimentary Geology.)

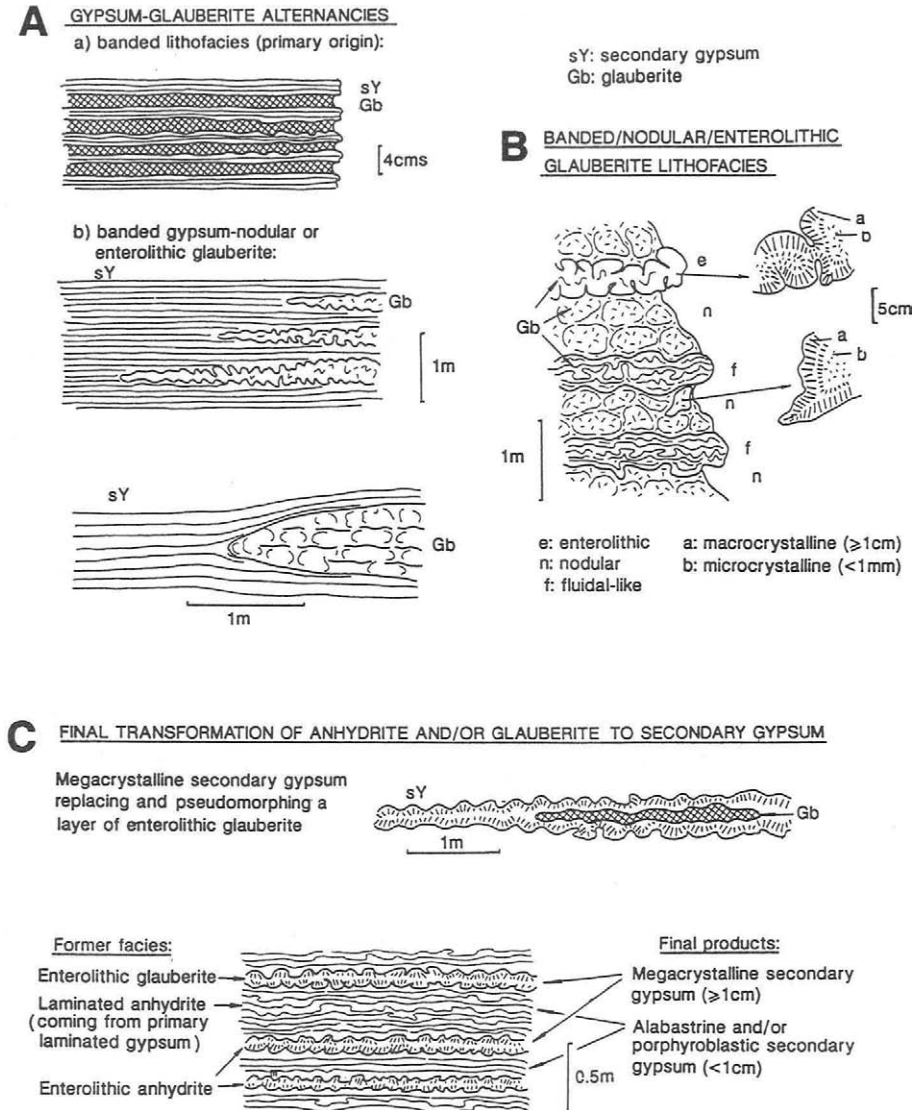


Figure 2.13 Various forms of glauberite and gypsum/anhydrite found in the Alcanadre area. (From Orti and Salvany, 1990; courtesy of Dr. Orti.)

At *Alcanadre* the glauberite has been described as occurring in three forms (Fig. 2.13): (1) thin (20–30 cm thick) beds of nodules arranged in intricate micro-fold structures (called enterolithic: small intestine-like folds that originate through chemical changes resulting in a swelling of the newly formed mineral), interbedded

with laminar gypsum; (2) thick 1–4 m layers with well-defined internal beds of massive glauberite; or (3) 1–4 m thick masses of laminated and elongated clusters (“nodules”) in an enterolithic pattern. These beds can contain fairly pure glauberite and are finely or coarsely laminated with the host rocks, gypsum, clay, and marl. The three forms of glauberite often alternate, with the upper half of the beds usually containing more laminations and being more deformed. In the lower half the crystal masses (nodules) have a more uniform shape and contain larger crystals. In the large nodules the crystal size commonly increases from the core to the edge, from $<500\text{ }\mu\text{m}$ to large (1–2 cm) euhedral crystals at the periphery (Salvany and Orti, 1994).

In the thin beds the glauberite is more pure and compact, made up of fine to medium-sized crystals, whereas the massive, laminated and banded glauberite in the thick beds is porous and fragile, with the glauberite in randomly oriented, variably sized (100 μm –3 cm) aggregates with gypsum, clay, and marl laminae and inclusions. The crystals are usually prismatic and rhombohedral and are commonly grouped into a subhedral or euhedral fabric. Fine crystals may also form larger masses several centimeters long. There are no soluble salt inclusions in the crystals, but the inclusion of matrix material (gypsum, clay, marl, etc.) is common, as if the crystals grew in place and trapped some of the surrounding mud. The mechanism of mirabilite or a stratified or interstitial strong sodium sulfate brine being met by a high-calcium groundwater in the bottom of a shallow lake or in playa sediments to form some of the massive glauberite would appear to be strongly indicated by the petrographic studies of this deposit. Other portions of the glauberite were inferred to have been formed by the replacement of gypsum with high-sodium-sulfate waters because of their enterolithic structure and numerous matrix inclusions (Salvany and Orti, 1991).

Gypsum is the major matrix mineral in this formation, formed by the rehydration of anhydrite or the replacement of other sulfates. In the latter case it occasionally is only present in the outer area of the converted mineral and remains as anhydrite in the center, or appears as pseudomorphs of the original mineral. It occurs in lenticular, laminated, or nodular-enterolithic forms, with the lenses composed of large crystals or aggregates of smaller crystals. The laminar form is made up of small crystals that deposited on the floor of the saline lake, with wave ripples and other bottom features preserved during dehydration and rehydration. The enterolithic nodules appeared to have formed in place during the hydration of anhydrite while still moderately deeply buried and under compression. The nodules, lenses, and laminae were all originally deposited as gypsum, and were later converted to anhydrite by strong brine and higher temperatures, and/or upon deep (>500 – 1000 m) burial. The anhydrite that was formed was usually fine-grained (30–50 μm), white or blue, and had an unoriented prismatic fabric pattern. The rehydration of the anhydrite to gypsum occurred comparatively recently as the formation was raised to a position where groundwater could reach it to make the conversion. Some gypsum was also formed by the leaching of glauberite or polyhalite.

Other Minerals

Polyhalite is fairly common in the deposit, occurring with any or all of gypsum, glauberite, halite, and carbonates, and often as thin (millimeter thick) layers with any of the matrix minerals to form centimeter-sized bands. It was formed by the replacement of fine-grained gypsum, anhydrite, or glauberite, and consequently pseudomorphs of these minerals are common. Its spherulite crystals range in size from 200 μm to 2 mm and are usually very pure and difficult to distinguish from fine-grained gypsum. Polyhalite can also occur along halite crystal boundaries, with the halite forming beds in the Lerin Formation centimeters to decimeters thick, interlayered with laminated gypsum. Thicker halite beds have been formed in the earlier Falces and Zaragoza Gypsum Formations. The crystals are millimeter- to centimeter-sized, of a zoned hopper structure, and contain many small inclusions of fluid, anhydrite, and polyhalite.

Dolomite is quite common and is the dominant carbonate mineral in the formation, although magnesite is the only carbonate found with glauberite and polyhalite (in contrast to the Rio Tiron area, where only dolomite has been reported). Both carbonates can occur as several-centimeter-thick massive or laminated beds and appear to have been formed by the replacement of calcite by high-magnesium brines. The clay in the formation is composed of illite and chlorite, with lesser amounts of kaolinite, and it is usually mixed with considerable dolomite (Salvany and Orti, 1994, 1991).

In an earlier article the stratigraphy of the *Alcanadre* (Rioja, or *Ermita de Aradon*) mine has been described (from the base up) as 25 m of reddish and greenish-gray clay with gypsum, 2 m of gray clay with gypsum, 2 m of glauberite and gray gypsum (40.3% Na_2SO_4 in one sample), 1 m of alternating layers of gypsum and clay, and 3 m of glauberite and gypsum (44.5% Na_2SO_4). No thenardite was observed, and the overburden consisted of 60 m of saccharoidal gypsum beds alternating with clay, showing signs of considerable leaching (Ordóñez *et al.*, 1982). This mine was operated during the early 1800s and was located along the Ermita de Aradon road. At that time thenardite was reported to have been its ore, with the primary sales being for the production of sodium carbonate (for the LeBlanc process; Ordóñez and García del Cura, 1992; Rios, 1968). At *San Martín de Berberana* (municipality of Agoncillo) two layers of glauberite were being mined in 1982 from a deposit that appeared to be similar to that at Ermita de Aradon. North of the Ebro River in Navarra there also are many areas with similar outcrops (Ordóñez *et al.*, 1982).

Remolinos–Zaragoza Area

In this area of Zaragoza province to the southeast of the Ebro Basin there are less massive deposits of glauberite, and the area is better known for its sodium chloride mines near Remolinos. One halite deposit contains about 16 million tons of halite, and in 1984 50,000 t/yr were being mined (Menduina *et al.*, 1984). Drilling in the La Real salt mine has encountered some beds of glauberite that occasionally contain zones of thenardite (Orti and Salvany, 1991). Core samples taken from the

mine indicated a 3.2 m glauberite bed at a depth of 86.4 m. A second core 100 m away encountered a 30 cm layer of glauberite at 59 m depth, and >26 m (to the end of the core) of glauberite at 80 m depth (Ordóñez and García del Cura, 1992). In another core (called the Purasal) there were four glauberite beds 3.1–6.5 m thick (totaling 16.5 m of glauberite) in a 25.5 m zone, with interbeds of shale or halite. The glauberite zone was beneath massive beds of halite (García-Veigas *et al.*, 1994). The mining company Tolsa announced a major find of glauberite near Zaragoza (Anon., 1985) that in places was more than 30 m thick and averaged in excess of 43% Na_2SO_4 . Layers of thenardite were also reported, and a production feasibility study was made on the deposit. However, as of 1999 there had been no commercial development, and it has been speculated that the reserves were not large and/or contained considerable halite (Orti, 1999).

Calatayud Basin

No publications have been made on glauberite in the Calatayud Basin (a small, narrow basin just south of Zaragoza), but highway cuts have exposed massive layers of anhydrite that had been formed from glauberite (Orti *et al.*, 1995). The glauberite was in the form of both nodules and enterolithic layers, and interbedded with anhydrite. At least one drill core in the area has been reported to have encountered major beds of fairly pure glauberite at a moderate depth, but it is not known if the deposit could be commercially attractive. The zone below the glauberite contains anhydrite nodules and boulders (Orti, 1999). Ordóñez and García del Cura (1992) also noted outcrops along the highway from Calatayud to Soria.

TURKEY

Cayirhan (Also Called the Kirmir or Beypazari) Deposit

This thenardite–glauberite (Na_2SO_4 – $\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$) deposit occurs in the upper section (the Kirmir Formation) of the Neogene Beypazari–Cayirhan Basin. The basin is in the Central Anatolian Plain near Ankara in northern Turkey, extending between the towns of Urus and Sاریyar. It has a maximum thickness of 1200 m and can be divided into seven quite unusually different stratigraphic units (Fig. 2.14). The lowest unit contains a lignite deposit, the next lowest (the Hirka Formation) has a trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) deposit, and the upper unit (the Kirmir Formation) a soluble sodium sulfate deposit. The Kirmir Formation can be up to 250 m thick, and the soluble sulfates occur in the second from the bottom of its four zones. The other zones consist of gypsum or gypsiferous sediments, with claystones and mudstones containing abundant gypsum crystals and fissure fillings (a “gypsiferous claystone”) below the glauberite–thenardite beds, and above them is 60–70 m of gypsum.

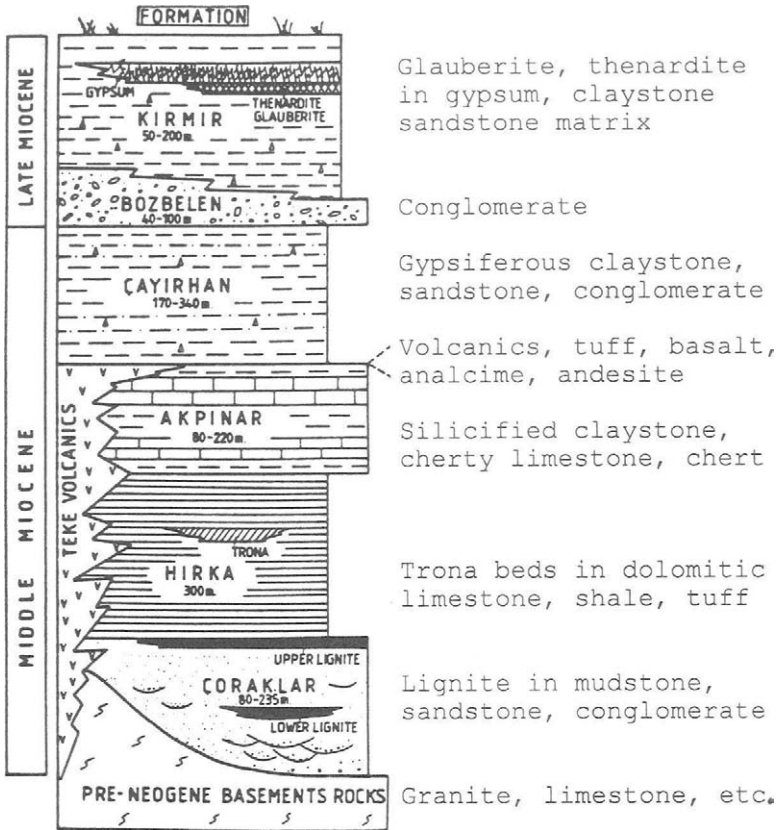


Figure 2.14 Generalized stratigraphic section of the Neogene deposits in the Beypazari Basin. (From Yagmurlu and Helvacı, 1994; reprinted by permission of Blackwell Science Ltd.)

The soluble sodium sulfate horizon (Fig. 2.15) outcrops in the Kirmir Valley and is 9–30 m thick (8–25 m, Celik *et al.*, 1987), lying between the Late Miocene or Pliocene Ucyatak and Softe units of the Kirmir Formation. In the outcrop area 1 cm–2.65 m thick beds of thenardite and glauberite alternate with layers of shales, claystone, or mudstone. Other areas of the deposit, however, consist of a bedded lower unit and a massive upper unit, with an uneven boundary between them (Orti *et al.*, 2000). The thenardite beds are usually perfectly flat, 1 cm–1 m thick, may have some dissolution cavities, and the crystals are large with a transparent, glassy, or milky appearance. The crystals are 1–100 mm long, with a white or light blue color, and a sub- to euhedral habit. Occasionally, such as in mixed glauberite–thenardite beds, the crystals are elongated and in a nearly vertical position, as if deposited in that manner. In areas of dissolution–recrystallization, the thenardite occurs as masses or layers of large (up to several decimeters long), very pure, transparent

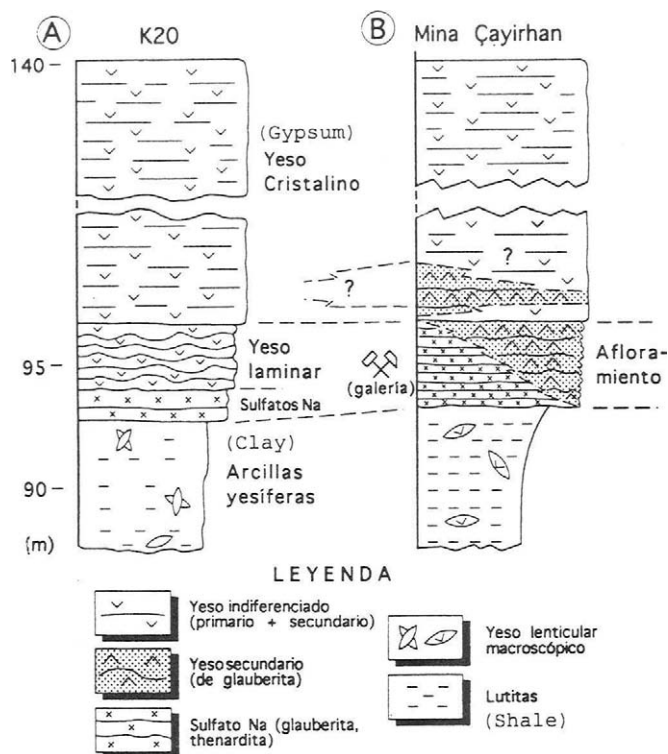


Figure 2.15 Stratigraphic section of the Bepazari glauberite deposit. (From Orti and Helvacı, 1995; reprinted by permission of Sociedad Geológica de España and *Geoacta*.)

crystals with a cemented appearance. The texture of the thenardite (and much of the glauberite) suggests that it was derived from mirabilite and later transformed into its present state. The estimated thenardite reserves are about 1 million mt, with an ore grade of up to 93% Na_2SO_4 (Orti *et al.*, 2000; Orti and Helvacı, 1995; Yagmurulu and Helvacı, 1994; Celik *et al.*, 1987).

The glauberite formation covers a much larger area and thickness than the thenardite, and both are only found in the center of the basin. The glauberite beds are of two types. One type has thick, massive layers of large clear, earthy, or milky crystals forming aggregates, often with abundant thin clay-carbonate interlayers, and there are some flattened glauberite nodules. The second type has relatively compact and pure laminated beds of small, dark-colored crystals. The glauberite crystals are usually earthy or milky colored, of a prismatic-tabular shape with a variable < 1 mm to > 1 cm size, in aggregates, and with frequent solid inclusions. Their crystal fabric appears to have been both disoriented and reoriented during their initial formation, as if by uneven compaction or dissolution and regrowth. Although

much less common, some crystal groups occur as nodules or in a fan shape, with impurities in the center, and the crystals are slightly curved. There are also some glauberite dissolution zones with beautiful, clear crystals. The fine laminae of clear glauberite contains transparent, anhedral crystals and has the appearance of a primary mineral deposited within a lake. The majority of the glauberite textures, however, appear to be those of interstitial growth within a clay–magnesite matrix. Isotopic data indicates that the sulfate in the thenardite and glauberite is of marine origin, although the deposits are clearly from inland lakes (Orti *et al.*, 2000).

When glauberite occurs with thenardite there often are glauberite beds above and below the thenardite layers, and both usually are quite pure. However, sometimes there can be a 10–50 cm mixed thenardite–glauberite–shale transition layer between the separate beds, and thenardite occasionally is present as a cement between glauberite crystals in this zone. Disseminated glauberite crystals are also commonly present in the gypsum beds above and below the thenardite zone. In the outcrop areas the thenardite has been dissolved and the glauberite converted to laminated gypsum for a distance of several meters. There is considerable sodium sulfate efflorescence on the surface, and gypsum pseudomorphs of glauberite. The associated clay minerals in the deposit are smectite and illite, both in the calcium form (Orti and Helvacı, 1995; Yagmurlu and Helvacı, 1994). Exploratory mining has been done on the deposit (Fig. 2.16).

A chemical analysis of the formation's minerals is listed in Table 2.2. It indicates the presence of sodium carbonate, but since gypsum and glauberite are comparatively soluble, calcium carbonate would immediately precipitate if both calcium and carbonate ions were present in the crystallizing solution. An error in the analyses is further indicated by the low values for the presumed fairly pure crystals of each mineral that were analyzed. The glauberite reserves are estimated to be 190 million mt, containing about 65 million mt of Na_2SO_4 (Alkim, 1999).

UNITED STATES

Arizona: Camp Verde

The Camp Verde thenardite (Na_2SO_4) deposit in Yavapai county is located about 2 km west of the town of Camp Verde (an old military post) in the Verde River valley, outcropping along the side of Copper Canyon (Fig. 2.17). It is the largest and best known of the United States' ancient, buried sodium sulfate formations, and also probably the earliest underground mine workings in the United States. There are indications that tunnels had been made into its halite outcrops (some halite is interbedded with the thenardite) perhaps 2000 years ago. Then during the 14th and 15th centuries it became more intensively worked, with a few thousand yd^3 of salt having been removed. Many artifacts of this period, including cedar bark torches, sandals, stone picks, and pick handles, have been found in the tunnels, as well as the mummified body of

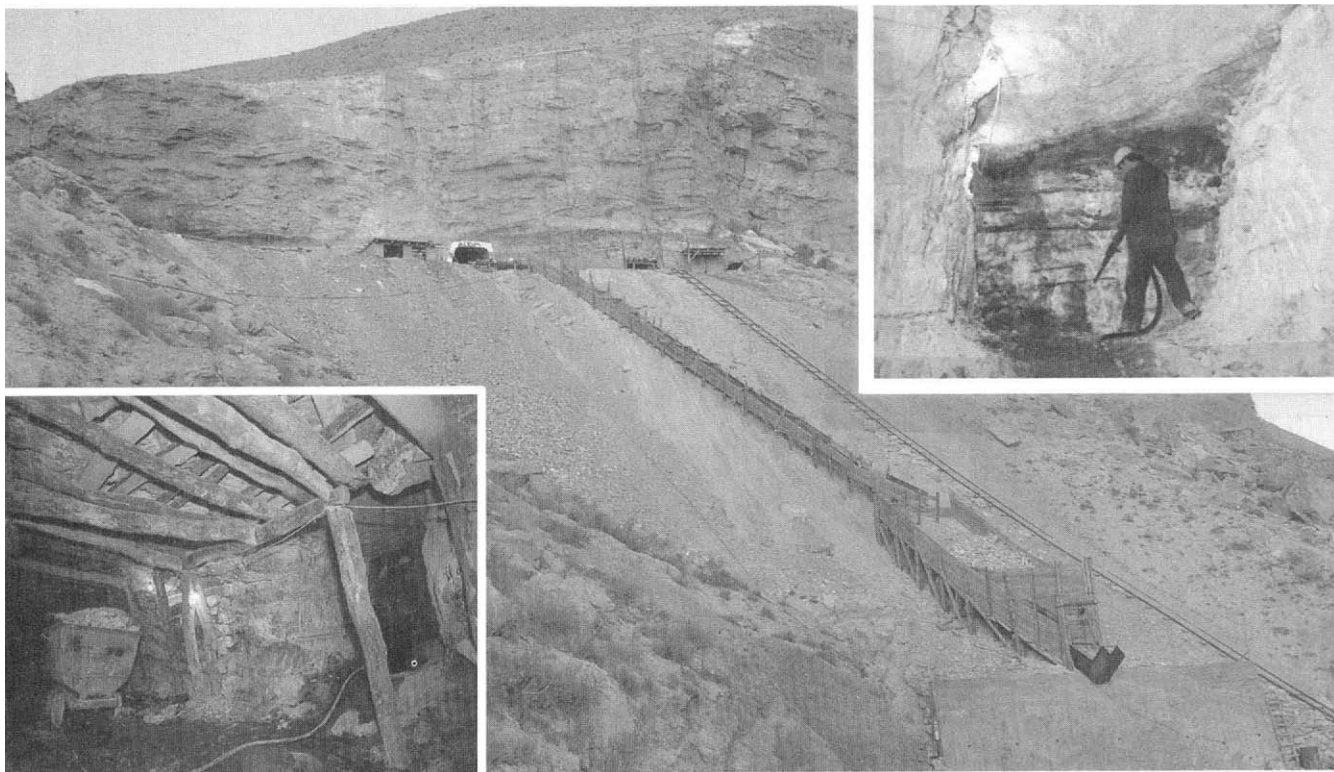


Figure 2.16 Exploratory mining at the Beypazari glauberite deposit. (Alkim, 1997; reprinted by permission of Alkim Alkali Kimya Anonim Sirketi.)

Table 2.2
Analyses of Core Samples from the Cayirhan Deposit in Turkey (wt %)^a

	Thenardite		Glauberite	Gypsum
	NS4-1	NS4-2		
Thenardite	76.77	70.88	—	—
Glauberite	—	—	63.56	—
Gypsum	—	—	—	81.50
Na ₂ CO ₃ ^b	10.31	26.14	15.51	—
CaCO ₃	11.71	1.33	14.29	12.45
MgCO ₃	0.71	0.66	4.37	3.08
Excess CO ₂	—	0.88	0.01	0.03
NaCl	0.07	—	—	—
SiO ₂	0.26	0.00	1.11	0.96
Al ₂ O ₃	0.00	0.00	0.40	0.25
Fe as Fe ₂ O ₃	0.01	0.01	0.15	0.13
K ₂ O	0.00	0.01	0.04	0.06
H ₂ O	0.16	0.09	0.56	1.47

^aYagmurlu and Helvacı (1994).

^bValues appear to be in error, since soluble carbonate would indicate the presence of burkeite, and none has been reported, or the carbonate would have precipitated with the (soluble) gypsum.

a miner trapped in a cave-in. The salt appears to have been an important food and trading commodity for the local Mesa and Rio Verde cliff-dwellers.

The area of the deposit had experienced complex faulting and volcanism during the mid-Tertiary period, with volcanic flows forming a closed basin during Miocene times. Sedimentation with some continued volcanism then proceeded to fill the basin, including the deposition of massive lacustrine limestone in its central area. As the lake water periodically evaporated to a much higher concentration, gypsum, halite, and thenardite were also deposited in the basin's center. The closed valley opened by early Pleistocene time, and erosion became the dominate process in this Verde Formation, resulting in outcrops of the thenardite deposit in its southeast corner (Thompson, 1983). The deposit covers about 7 km² and appears to contain about 100 million mt of equivalent sodium sulfate. The thenardite zone averages about 20 m (65 ft) in thickness, with this section containing 73.2% sodium sulfate, 15.4% halite, 10.2% insolubles, 1.6% calcium, and 1.2% magnesium (Table 2.3). The beds are fairly level, or have only a modest slope, and appear to be generally continuous over the extent of the deposit (Garrett, 1968).

The thenardite is found in beds of variable thickness and purity, ranging from being almost totally pure to heavily contaminated with either or both halite and clay. There are also interbeds of predominately halite or clay, with most of the halite near the base of the deposit. Some of the lower fairly pure halite beds are up to a meter

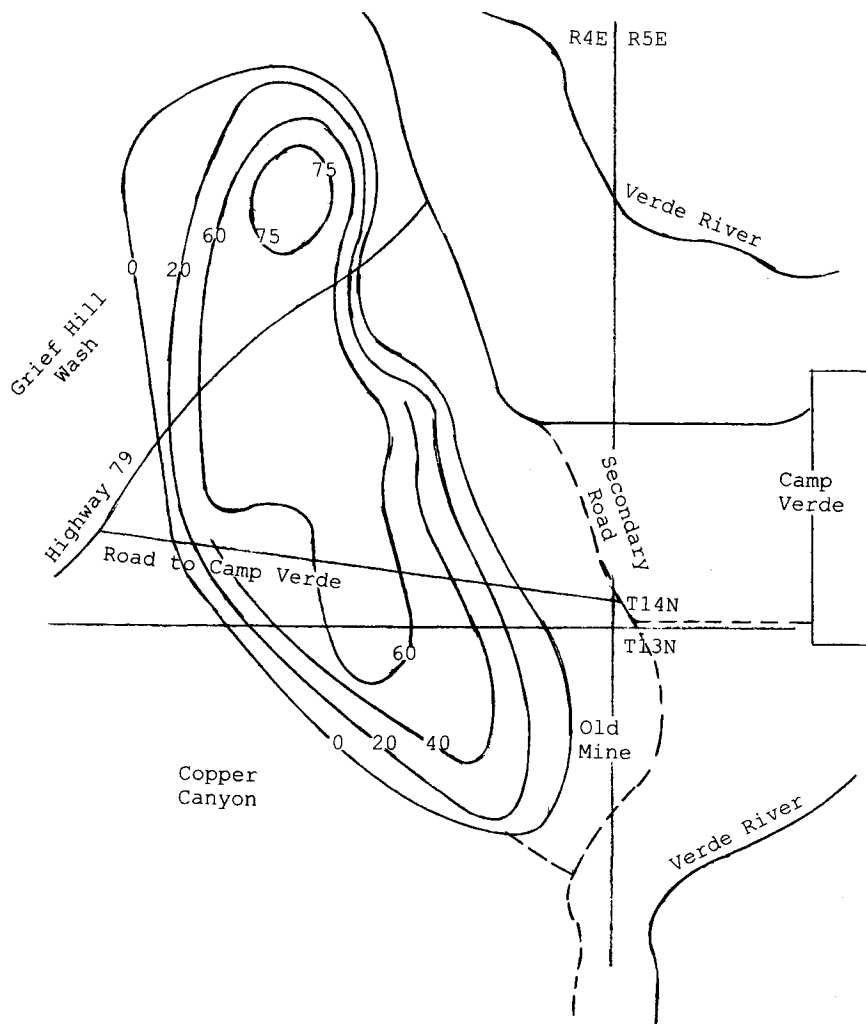


Figure 2.17 Isopach map of the ore thickness at the Camp Verde thenardite deposit ($>70\% \text{Na}_2\text{SO}_4$, in feet).

thick, and these were the ones mined by the local Indians. The deposit also contains “beautifully transparent masses (of halite) sparingly disseminated” in the thenardite, and some of the halite has a brilliant blue color. The outcrop area of the deposit consists of “a series of rounded hills with sides covered with a snow-white efflorescence” of thenardite–mirabilite. Within the deposit the thenardite is coarsely crystalline, compact, and hard, requiring drilling and blasting to be broken and removed. Some of it is contaminated with a greenish clay, but large masses are also colorless and transparent with a slight yellowish tint, and they seldom show a crystalline form.

Table 2.3
Thickness and Analysis of Several Cores from the Camp Verde Thenardite Deposit^a

Location	Ore, ft		Chemical Analysis, wt %			
	Depth	Thickness	Na ₂ SO ₄	NaCl	Insol.	Ca
1	85	75.5	69.4	18.7	11.9	—
2	66	56	84.3	1.7	12.7	1.3
3	82	57	71.9	17.8	8.9	1.4
4	90	60	78.3	9.0	12.7	—
5	94	56	70.4	18.8	8.4	2.4
6	60	88	71.1	19.1	8.4	1.4 ^b
7	22	64	67.3	22.7	8.6	1.4
Average	71.3	65.2	73.2	15.4	10.2	1.6 ^b
(meters)	21.7	19.9				

^aGarrett (1968).

^bAlso 1.2% Mg. The deposit runs in a NNW direction, and is about 1.4 km wide and 5 km long.

The samples are roughly:

1. 0.4 km from the west, 0.7 km from the north edges
2. 0.4 km from the east, 0.9 km from the north edges
3. 0.35 km from the west, 1.7 km from the north edges
4. 0.1 km from the west, 2.2 km from the north edges
5. 0.35 km from the west, 2.5 km from the north edges
6. 0.3 km from the east, 1.0 km from the south edges
7. 0.2 km from the east, 0.3 km from the south edges (near the outcrop).

There are some veins of mirabilite (Na₂SO₄·10H₂O) above the deposit in the overlying beds, and it extensively occurs in the outcrop areas in zones up to a meter thick. There is also some glauberite (Na₂SO₄·CaSO₄) in the clay within and over the deposit, but it primarily occurs in a thin bed at the deposit's base, and in a limited zone of clay under the deposit. The glauberite is in the form of clear, transparent colorless crystals, generally as thin shafts 1.3–2.5 cm across and 3–6 mm thick, but varying greatly in size and habit. Glauberite crystals occasionally occur in the thenardite or halite as inclusions, and they in turn often contain small liquid inclusions. When the glauberite outcrops it has frequently been transformed into calcite pseudomorphs, many of which make excellent collector specimens (Blake, 1890).

California: Bertram

The *Bertram* (also called the *Durmid Hills*, or *Imperial Valley*) thenardite–astrakanite (Na₂SO₄–Na₂SO₄·MgSO₄·4H₂O) deposit is probably the most distorted, faulted, and partially leached of the world's large, old buried sodium sulfate deposits, having the misfortune of being located between two branches of the very active San Andreas Fault. Aerial photographs show that it outcrops over about a 2.6 km² area in the Durmid Hills, northeast of the Salton Sea, 2.4 km north of the Bertram rail station. However, a modest drilling and trenching program has only been done on

about one-fourth of that area. These studies indicate inferred reserves of about 2 million tons of sodium sulfate, with about 20% of that occurring as massive beds, and the remainder as disseminated thenardite crystals (visually identified in drill logs) in clay containing ~20% Na_2SO_4 (Fig. 2.18; Garrett, 1963).

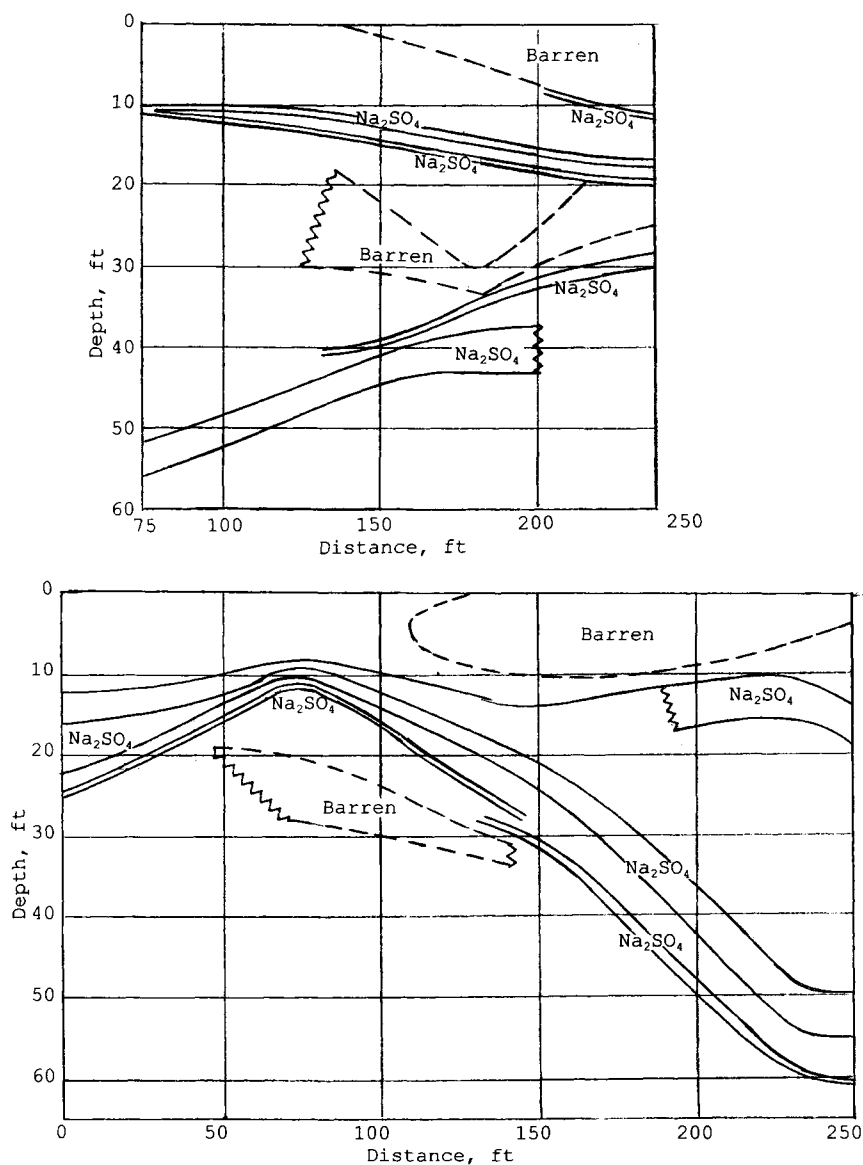


Figure 2.18 Cross-section drawing of two zones in the Bertram thenardite-astrakanite deposit.

The deposit was formed in sandstone–clay–gypsum lacustrine sediments, which after undergoing extensive seismic movement had its surface planed off to form a relatively smooth sloping desert floor below the former beach line of possibly an intruding late Miocene–early Pliocene sea, and then a Pleistocene lake. This surface has subsequently been deeply eroded to form rough foothills along the base of higher mountains to the east, and the sodium sulfate outcrops are now about 30–38 m below sea level in the Salton Sea Trough (Tucker, 1924; Garrett, 1963). The sulfate-bearing zone is about 67 m thick, resting on and overlain by finely bedded gypsiferous silts. The strata, from the bottom upward, contain the following: 7.6 m of gray clay that appears saline at outcrops after rains; 7.6 m of conspicuous red sandstone containing fine, loose, friable micaceous grains; then a 34 m sodium sulfate zone; and finally 18.3 m of brown-weathering sandstone, easily recognizable at outcrops by forming low ridges.

The frequent sodium sulfate outcrops are a mirabilite–thenardite–insolubles mixture, usually less than 1 m thick, and fairly stable from the area's infrequent rains. A small amount of mirabilite is also found in thenardite–astrakanite beds, in pockets, cracks, and occasionally as occlusions. Near the surface the sodium sulfate beds (called “ledges” in this deposit) are quite pure thenardite (>99.8%), but with depth they appear to grade into astrakanite mixtures, with up to 55% astrakanite in the base of one 13.7 m trench, perhaps implying more astrakanite at greater depth. The thenardite is hard, almost glassy to finely crystalline in solid beds up to about 2 m thick. Both above and below the main bed there may be several thinner beds 20–40 cm thick, separated by up to 1.2 m of clay. Some of the thenardite is interbedded with thin shale layers, and the main bed is often about 11 m above the underlying red sandstone. Most of the clay in the 34 m sodium sulfate zone contains a considerable content of disseminated thenardite crystals, varying from 10 to 40% Na_2SO_4 , and averaging about 20%. The saline clay under the red sandstone was not analyzed, but may also contain sodium sulfate. Sodium chloride is essentially absent in this deposit (Gale, 1942).

Only limited drilling and trenching has been done in the area, with no drill holes deeper than 46 m, and many were only 16.8 m deep. Also, only a few comparatively short lines of holes were made, so the data are very limited. However, with the shallower drilling a few leach (barren) zones were indicated, a gentle anticline structure of the thenardite beds was shown, and the beds appeared to have a variable continuity and extent. With the deeper drilling both anticlines and synclines were found, with the structure thickening and flattening to the west. Some of the structure of the deposit has also been inferred from several mining trenches that were made into the outcrops (Garrett, 1963).

The first production from the deposit was conducted from November 1922 to June 1923 by E. H. Otto and Company, who shipped 2300 mt of sodium sulfate. The mining was done by trenching along an outcrop with a 183 m long, 4.3 m deep pit (Fig. 2.19) that had a N 70° W strike in the eastern part of the deposit. Three parallel beds were mined that had a 30–40° dip and were about 1.2 m apart and

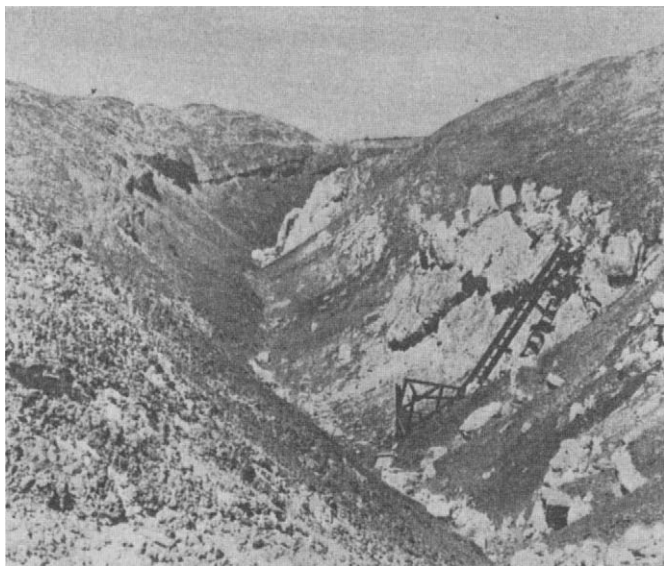


Figure 2.19 One of the trenches made to mine the Bertram thenardite deposit. (From Ver Planck, 1956; reprinted by permission of the California Department of Conservation, Division of Mines and Geology.)

0.46–1.22 m thick. In the west end of the trench the beds joined to form a thicker, 1.83 m bed. About 820 m west of the main trench a second one was made about 61 m long and also 4.27 m deep. It encountered two thenardite beds, each about 0.61 m thick and separated by 1.22 m of clay. Much later the overburden-tailings dumps from the trenches were analyzed, averaging 12% Na_2SO_4 (Tucker, 1931, 1926, 1924).

In 1940 a second operator, the American Sulfate Company, shipped 230 mt of sodium sulfate from the deposit. They mined in the deposit's western area, with shallow trenches and pits first made along a 305 m outcrop line with a $\text{N } 70^\circ \text{ W}$ strike; then the mining was done in a 216 m long, 13.7 m deep trench in its western end. The thenardite bed in this area averaged 1.52 m in thickness and dipped at 65° S . Upon examination the deeper thenardite contained considerable astrakanite (28–56%), and the product that was shipped averaged 4% MgSO_4 (11% astrakanite). Because of magnesium's detrimental effects upon pulp making, the operation was then permanently suspended. A small crushing plant had been built with a capacity of 50 t/day. Ore was hauled from the pit in 5-t trucks, dumped into a hopper, and then crushed in a Climax jaw crusher to a 19–25 mm size. The discharge was screened in a 1.1×3 m rotary trommel with 3.2 mm openings, and the oversize crushed in a 5 t/hr hammer mill and rescreened. The -3.2 mm product was then hauled in 5-t trucks to the rail station at Bertram. The operation employed two men

and had a bulldozer, two 5-t trucks, and a rotary core drill. and air compressor (Sampson and Tucker, 1942).

Nevada: Virgin River

A glauberite deposit has been reported 7.2 km southwest (8 km south; Vanderburg, 1937) of St. Thomas, northwest of the Hoover (Boulder) Dam, and on the west side of the Virgin River valley. It was called the *Stewart deposit* and was in the Muddy Creek Formation of Pliocene age. Unfortunately, it was flooded by Lake Mead as the Colorado River water backed up behind the dam. It had outcropped on a steep slope 24–30 m above the river, and continued for 460 m parallel to it. Both a 61 m adit driven into the bed and a 12 m vertical pit near the end of the adit remained in the ore. A quite uniform, pure, solid crystalline bed was exposed that contained an estimated 2–4 million tons of glauberite in the mined area. Samples indicated that the ore averaged 46.8% Na_2SO_4 (91.6% glauberite), 45.85% CaSO_4 (a 1.06% excess over that in glauberite), and 7.35% impurities (including insolubles and NaCl; Papke, 1976; Vanderburg, 1937; Carpenter and Smith, 1932).

This area also contains the adjacent massive Big Cliff, or Virgin Valley halite deposit, with a high (an average of over 3%) glauberite content. This lacustrine deposit was located from 16 to 40 km south of Overton, it had outcrops over a 64 km distance, and the halite in drill cores was 300–520 m thick. All of its outcrops, except two south of Overton Beach have also now been covered by Lake Mead. The deposit's size and shape are entirely unknown, but it appeared to be in the form of a gentle anticline. The halite was coarsely crystalline, and much of it may have been recrystallized. However, in some zones layers of glauberite, clay, and tuff provided some evidence of bedding plains. The halite's average purity was about 93% NaCl, with the impurities consisting of "grains, blebs and interstitial masses of glauberite, sand and silt between and within the 0.6–1.3 cm salt crystals." Locally there were masses of large, exceptionally pure salt crystals. The glauberite occurred as sacroidal to coarsely crystalline beds, and as "euhedral crystals of plowshare habit up to 5 cm long dispersed or interlocked in halite and siltstone. The euhedral crystals were randomly oriented, although near vertical attitudes were perhaps most common. Fine intermixtures of silt and glauberite presented a speckled brown and white appearance." In many areas the glauberite had been leached to form gypsum, especially near the outcrops, and there were many gypsum pseudomorphs after glauberite. There was almost no calcite, primary gypsum, or anhydrite in the deposit, and it contained very little magnesium, potassium, or sulfides. The glauberite gave the appearance of having crystallized with the halite (Mannion, 1963).

A third sodium sulfate occurrence in this area has been reported 20 km to the southwest in the *Muddy Mountains* (in the White Basin and Bitter Springs Valley), about 4.8 km south of a large colemanite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$) deposit. It outcrops along the side of a prominent cliff and was said to be "intimately associated with

siliceous impurities" (Vanderburg, 1937; Carpenter and Smith, 1932; Longwell, 1928). In a totally unrelated area, glauberite and halite have also been reported in the Triassic rocks of central New Jersey (Hawkins, 1933).

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Chapter 3

Recent Lake, Playa, or Surface Deposits

ANTARCTICA

Hobbs Glacier

One of the world's most unusual occurrences of sodium sulfate is in the scattered large and small deposits and numerous surface crusts of mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and thenardite (Na_2SO_4) found in Antarctica. By far the largest such accumulation of mirabilite is the bedded outcrops in a 5 km^2 area of the moraine (its rocks and sediments are 30–100 m thick on top of an ice sheet; this is called “ice-cored”) between the terminus of the Hobbs Glacier and the coastline. (Fig. 3.1; Bowser *et al.*, 1970). An estimated 10 million mt of mirabilite are present in this area (Keys and Williams, 1981). Almost 160 outcrops of the deposit have been examined, and 19 more were noted in aerial photographs, with the individual outcrops 1–50 m (more than 30% >7 m) long and the beds 0.04–4 m thick. They range from pure mirabilite (the larger ones) to mirabilite-cemented till, and both are associated with (and sometimes covered a few centimeters by) uncemented till, well-sorted sand, and/or algal mats or peat (Fig. 3.2). There are faint lines within the mirabilite beds indicative of seasonal laminations, and with all of the Antarctic deposits there is some surface dehydration of the mirabilite to thenardite, giving it a thin, powdery coating.

The mirabilite beds occur from sea level to almost a 200 m elevation, and some are found beneath the frontal scarp and enclosed within an underlying glacier. They appear to have been separated by the glacial flow, and some are folded, contorted, and deformed (Dort and Dort, 1970a,b,c). Brady *et al.* (1979) felt that these beds were the remnants of an earlier deposit formed by leached efflorescent sodium sulfate in freshwater pools on the expanded glacier during the Wisconsin glaciation period. Dort and Dort (1972), however, suggested that they formed directly from seawater (with some later dehydration–hydration) during earlier periods of much higher sea levels (and before isotactic rebound), based upon the presence of adjacent high marine terraces containing the remains of marine organisms. The younger algal mats

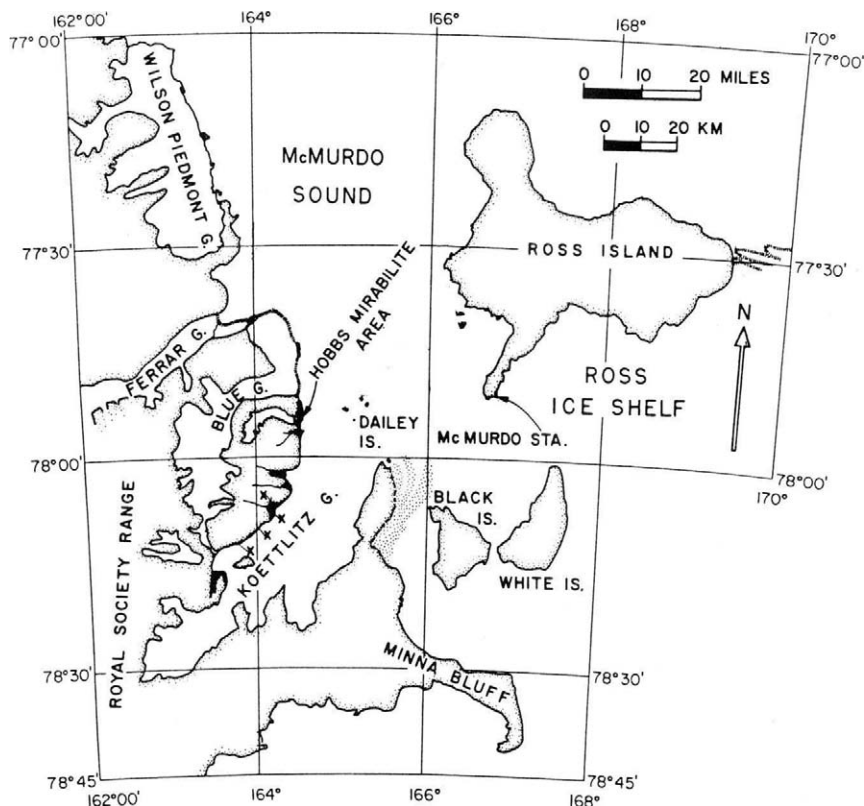


Figure 3.1 Some of the mirabilite deposits in the McMurdo Sound area of Antarctica. (Black areas and Xs). From Bowser *et al.* (1970); reproduced by permission of the Mineralogical Society of America.

on some of the deposits, and random summertime brine pools, formed later on the newly exposed surfaces.

Sodium Sulfate Source

Seawater appears to be the obvious source for most of the sodium sulfate in Antarctica, since its $\delta^{34}\text{S}$ values are the same as in seawater (Fig. 3.3), and essentially all of the sodium sulfate in the massive amounts of seawater that freezes each year is crystallized. Most of the mirabilite's $\delta^{34}\text{S}$ values are in the +18.5–22.2 range (seawater in the presumed depositing period [$<12,200$ yr] is about +20), although in a few areas the values varied from 2.1 to 12.3, indicating a mixture of sulfate sources, including some from oxidized H_2S or SO_2 in rain or snow, or leached sulfide minerals, sulfur or nonmarine gypsum, with assumed $\delta^{34}\text{S}$ values of +5 to –50. The

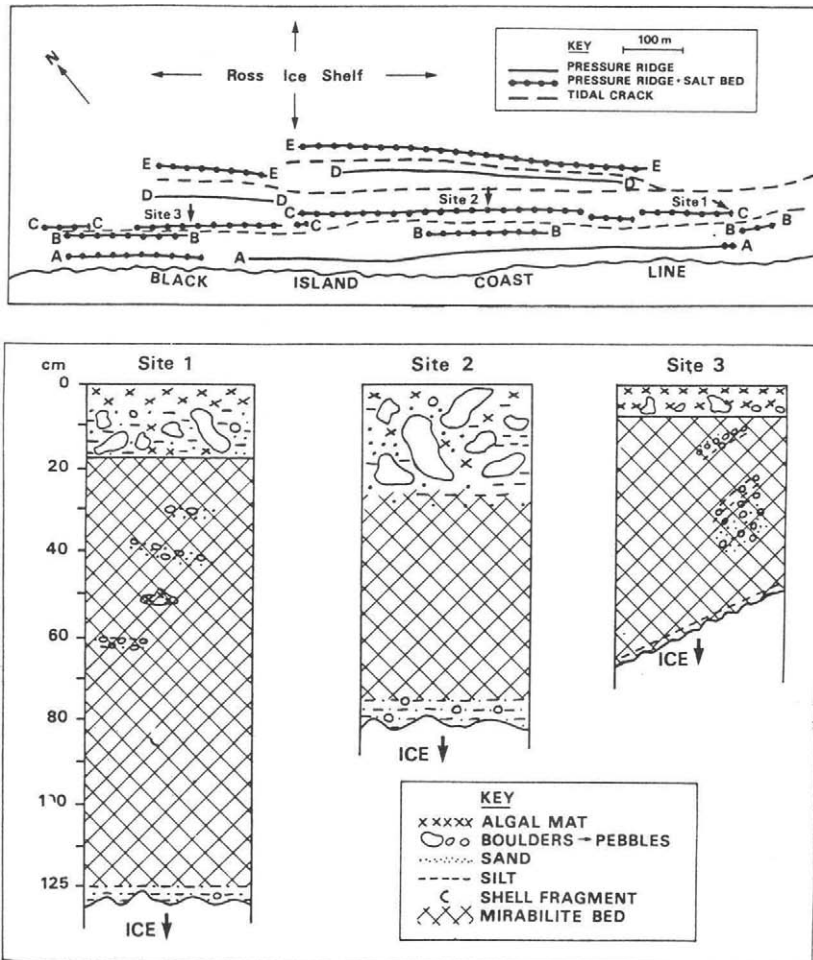


Figure 3.2 Stratigraphy of the Cape Spirit mirabilite beds. (From Brady *et al.*, 1979.)

mirabilite's $\delta^{18}\text{O}$ values are the same or lower than those of seawater, since presumably some of the water of hydration also fractionated as it crystallized. Partial mirabilite recrystallization with glacial water would have also caused a similar effect (Barkov *et al.*, 1995; Matsubaya *et al.*, 1979).

Other Deposits

There are also discontinuous mirabilite beds up to 1 m thick in a 1250×250 m area on the Ross Ice Shelf, called the Cape Spirit beds. They are underlain by up to 8 cm

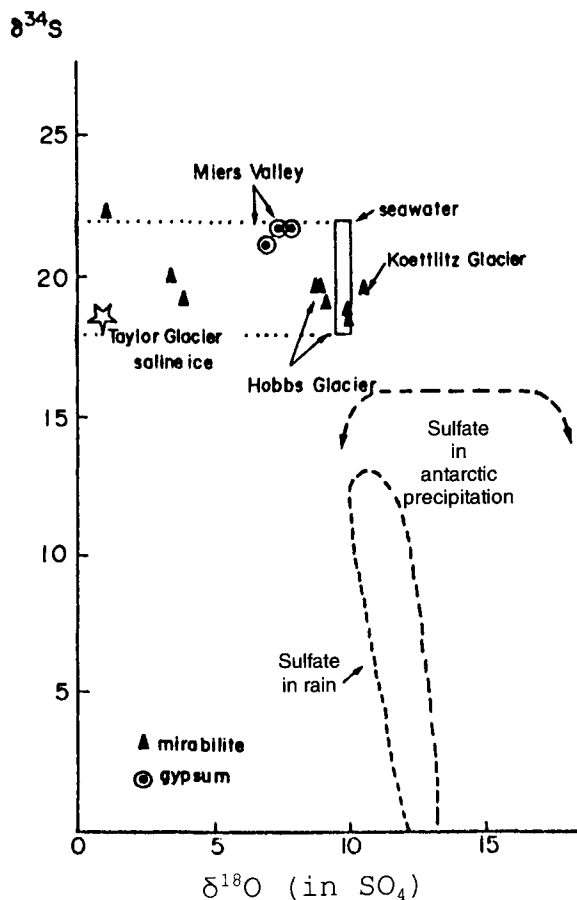


Figure 3.3 Typical Antarctic mirabilite isotopic data. (From Keys and Williams, 1981, *Geochimica et Cosmochimica Acta* Vol. 45, No. 12, p. 303; with permission from Elsevier Science.)

of marine mud (containing marine diatoms) and have nonmarine algal mats above them. There are nonmarine diatoms in both the mirabilite and the overlying mats, indicating that they were deposited from freshwater pools (or a lake) on the ice shelf. Brady *et al.* (1979) theorized that the lake resulted from melting ice containing mirabilite, and the underlying mud might have been forced through cracks and crevasses to the surface by the weight of the ice.

Dort and Dort (1969, 1970a,b, 1972) described a number of other mirabilite formations, such as in the Miers Valley (also Torii *et al.*, 1966). These are in horizontal beds, undisturbed by glacial movement, at an elevation of 150–250 m, and in some places accompanied by gypsum and calcite. About 8 km south a highly contorted and folded bed of mirabilite is exposed in the adjacent moraine

along the edge of the Koettlitz Glacier at a 200-m elevation. There are mirabilite beds within the stagnant ice of the glacier that have also been identified as marine in origin by isotopic evidence (Fig. 3.3). At Deep Lake in the Vestfold Hills there is a >1 m thick bed exposed over a 5×10 m area near the lake shore. In the Skarvs Nes district of the Prince Olaf Coast there are layers of mirabilite 2–30 cm thick interbedded with (marine) shell-bearing sand and laminated silt. They are exposed 1–2 m above the level of an unnamed highly saline lake. Deposits have also been noted 31 m above sea level at Cape Barne, and on one of the Dellbridge Islands.

Dort and Dort (1970b) also found mirabilite on the annually formed sea ice between the Black and White Islands. Elsewhere, “long windrows of accumulated (mirabilite) near the southern end of Ross Island, . . . and on each shore of McMurdo Sound” have been reported, indicating that perhaps 1 million t/yr are currently being deposited on McMurdo Sound. A number of smaller deposits have been noted elsewhere on the ice shelves.

Mirabilite Crusts

By far the most common occurrence of mirabilite and thenardite in the Antarctic, however, is in the form of efflorescences and encrustations on the surface, or accumulations just beneath it, of the area's boulders and rocks (Bockheim, 1997; Keys and Williams, 1981; Vennum, 1980). The crusts occur in nearly all of the ice-free areas of Southern Victoria Land, and sometimes on perennial snowbanks or even glacier ice. There is generally less mirabilite as the distance inland increases, except in the higher elevations, but this relationship is not conclusive. However, there is a very positive correlation with the number of occurrences of halite (and some of the other oceanic salts) with their distance from the sea. This relationship, along with the sodium sulfate's $\delta^{34}\text{S}$ values in most of the deposits (other than the inland lakes) being similar to that in seawater, implies a sea-spray aerosol, or trapped seawater, or both as the source of these deposits. More than 28 other minerals have also occasionally been observed, but the sulfates are the most dominant (including some burkeite [$2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$] and glauberite [$\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$]; Von Hodenberg and Miotke, 1983), along with lesser amounts of halite, gypsum, and calcite (Fitzpatrick *et al.*, 1990; Nishiyama, 1978).

Seawater Crystallization

At very cold temperatures (the mean annual air temperature in the McMurdo region is about -20°C), and after some concentration by either evaporation or the crystallization of ice, mirabilite is the first salt crystallized from seawater. For instance, when 88% of the water has been removed, mirabilite begins to crystallize at -8.2°C (Fig. 3.4; Nelson and Thompson, 1954). When less concentrated, lower temperatures are required. It can be assumed that the residual brine after mirabilite has been

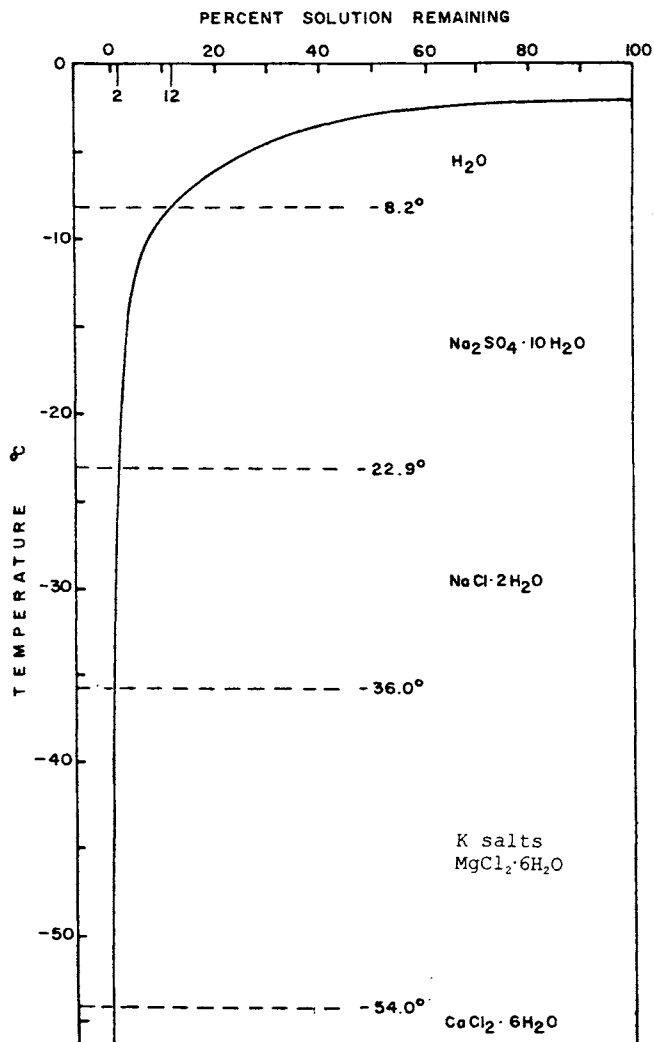


Figure 3.4 Crystallization sequence during the cooling of seawater. (From Dort and Dort, 1970a; by permission of the Northern Ohio Geological Society.)

deposited (containing mainly NaCl and MgCl_2 , the dominant salts in seawater) then eventually seep away. During the winter's colder temperatures some of the NaCl would also crystallize as the dihydrate ($\text{NaCl} \cdot 2\text{H}_2\text{O}$), but as the temperatures increased in the summer it would be the first salt to melt and redissolve, leaving sodium sulfate as the dominant crustal salt. A smaller amount of NaCl would also crystallize by evaporation during the summers. All but the most saline of brines freeze in

the area's winters, as exemplified by the very large ice shelf up to 4 m thick that forms in the oceans around the Antarctic each winter, and then largely melts during the summer. It has been estimated that a total of about 20×10^6 tons of salts per year are deposited on the Antarctic from sea spray carried by the continent's frequent storms and prevailing winds. Measurements of this aerosol indicate that the ratio of its sulfate to sodium content rapidly decreases as it moves inland, probably because of the sodium sulfate crystallizing in the manner just described, and then settling (Wagenbach *et al.*, 1998).

Deposit Thickness

If the bedded mirabilite deposits were formed directly from seawater, or inland lakes containing dissolved surface crusts of mirabilite, some means of repeated inflow must have been required to form the thick deposits (i.e., for 1 m of mirabilite 170 m of seawater would be required, which is far deeper than most basins could have been). Alternately, the thick deposits could have been formed directly from sea spray, or in shallow lakes that were repeatedly fed by redissolved sodium sulfate brine or fresh seawater, and then drained by overflow or seepage after crystallization. Convection currents caused by the summer's melted ice could have also caused such a new seawater flow in a density-stratified estuary. The increased concentration of brine in the lower sections would protect the mirabilite beds from dissolving in the repeated inflows of seawater until the upper brine concentrated, and more mirabilite was deposited. Finally, some flow from springs (in addition to the brine dissolved from previous deposits of mirabilite) must have helped to enlarge some of the deposits (Dort and Dort, 1970a). There is also evidence that some mirabilite deposits have been altered to a varying extent by microbiological activity (i.e., sulfate reducing bacteria; Barkov *et al.*, 1995). The Antarctic precipitation is <200 mm/yr, falling mostly as snow (Keys and Williams, 1981).

ARGENTINA

Pampa Region

The southern part of Argentina, as with most other desert regions of the world, has a large number of saline lakes or playas. Typically, most of them contain mixed salts or brines, and sodium chloride is the dominant crystallized salt. However, in a number of the deposits some mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) has crystallized with the halite (NaCl), or sodium sulfate is an important constituent (with the dominant halite) in the brine. Also, there are a few lakes or playas where mirabilite is the major salt crystallized, and others where sodium carbonate is dominant (but few with substantial amounts of magnesium sulfate or chloride). Some of the mirabilite deposits have been commercially operated, and the potential exists for sodium sulfate to be

Table 3.1
Analyses of Various High-Sulfate Lakes in Southern Argentina, wt% (Cordini, 1967)

	Million t						
	Na ₂ SO ₄	NaCl	MgSO ₄	CaSO ₄	Mg (HCO ₃) ₂	Insol.	Na ₂ SO ₄
Mirabilite analysis in the Sulfatera de:							
ChoiQUE (Nueva Roma)	95.30	1.34	0.78	0.52	0.18	1.87	0.22
Dreizzen	86.94	0.35	0.21	0.75	—	11.75	—
El Carmen	86.20	1.16	0.45 ^a	0.84	0.46	10.89	—
El Progreso (Vila Alba)	97.05	0.41	0.13 ^a	0.04	0.13	2.24	—
Br ^b	5.81	6.25	1.05	0.20	0.14	—	—
Salinas, or Salitral de (where NaCl is harvested):							
Arraraz (Crust)	94.03	3.21	0.04	0.20	—	2.52	—
Chasico ^c Br ^{b,g/l}	48.5	91.57	—	—	—	—	2.9
Cuerpos, Mirab. ^l	87.26	1.82	3.64 ^d	6.37 ^e	—	0.91	—
Daza, Mirab. ^l	64.35	34.41	0.16 ^a	0.41 ^e	0.64	—	—
Hidalgo, Glaub ^f (Grande),	47.70	0.21	1.05	48.41	—	2.63	4.8
Br ^{b,g/l}	10.83	288.8	1.29 ^a	5.02 ^g	1.61 ^h	—	7.3
Negro (Lote4) Br ^{b,g/l}	99.8	149.9	118.9	—	0.53	—	— ^j
Other Playas, Lakes:							
Callaqueo (Ast) ^k	54.11	2.58	41.02	0.96 ^h	—	1.33	—
Cominda (San	70.75	11.80	0.68	0.95	0.22 ⁱ	15.60	—
Marcos), Br ^{b,g/l}	67.65	127.1	0.26	1.63	0.49	0.26	—
Dominguez, Mirab. ^l	61.42	8.18	1.46	4.08	0.58	24.28	—
La Ernestina, Br ^b	1.90	1.26	0.25	1.74	0.02	0.05 ⁱ	97
Santa Rosa, Mirab. ^l	70.17	25.72	0.62	0.27	—	3.22	224

^aCa (HCO₃)₂.

^bBrine, g/l.

^cBuenos Aires province (the others are in La Pampa province).

^dNa₂CO₃.

^eNaHCO₃.

^fGlauberite.

^gMgCl₂.

^hCaCl₂.

ⁱK₂SO₄.

^jAlso, Colorada Grande contains 59 million tons of Na₂SO₄ (and 439 million tons of NaCl).

^kAstrakanite.

^lMirab. is a mirabilite bed.

an important by-product from a few of the larger salt operations. Table 3.1 lists the analysis of some of these high-sodium-sulfate lakes.

Among the lakes, the Salinas Grande de Hidalgo has a 0.8 m thick bed of fairly pure glauberite (Na₂SO₄·CaSO₄) lying between massive halite (above it) and mirabilite (below) layers, 1 m below the lake's surface. The lake has an area of 3000 ha, with 25–100 m of interlayered halite and mirabilite (average, 30 m thick). Laguna Callaqueo also contains a 0.3 m thick bed of astrakanite (Na₂SO₄·MgSO₄·4H₂O).

The highest purity of the bedded mirabilite occurs in the Sulfatera de Choique, but the playa is only 37 ha in size, with an average 0.47 m thick mirabilite bed (Cordini, 1967).

Bernasconi and Cangioli (1983) noted that during the period 1970–1983 the average Na_2SO_4 production from three of the southern provinces, Santa Cruz, Buenos Aires, and La Pampa, was 11,300, 6600, and 940 t/yr, but by 1983 it had tapered off to 1500, 0, and 0 t/yr, respectively (partly because of adverse weather conditions). About 50% of the product was converted to sodium sulfide at a plant in Comodoro Rivadavia to be used locally in curing leather. In Santa Cruz province there were four sodium sulfate operations in 1976 with total reserves of 1.2 million tons. All of the deposits in these provinces occur in relatively flat land with only low hills and gentle depressions, and the largest were Florentino Ameghino (Fig. 3.5) and Fatima II. In general they contained the following sequence of sediments: surface to 0.2 m, a crust of impure NaCl , Na_2SO_4 , and other salts; 0.21–0.4 m, clayey sand containing various salts (primarily sodium sulfates); 0.41–1.80 m, sodium sulfate mixed with dark clay; 1.81–>4.0 m (the depth of drilling), porous sodium sulfate.

The *Fatima II* deposit is located 51 km north of Caleta Olivia and 41 km southwest of Comodoro Rivadavia. The ore mined until 1983 was from an area with almost no overburden and was initially strip mined to a shallow depth. Later as brine seeped into the pit a floating dredge was employed to continue mining to a 4 m depth (the bottom was still in good ore). Wet ore was drained and dried at the edge of the pit, and a 10-year average analysis of the ore (on a dry basis) was 61.22% SO_4 , 31.43% Na, 1.68% Cl, 0.06% Mg, and 5.61% insolubles. During the 20 years preceding 1983, 100,000 t of product had been shipped, and an estimated 50 years of reserves remained.

The 13 km² *Florentino Ameghino* deposit is located at Pico Truncado, 56 km southwest of Caleta Olivia. The surface crust is a few centimeters thick, and under it there is a 0.3-m layer of mirabilite–thenardite, followed by 1.5 m of mud, and then another 1 m of sodium sulfates. There are numerous springs in and adjacent to the deposit. The average ore analysis from 1974 to 1983 was 57.34% SO_4 , 32.68% Na, 2.23% Cl, 3.08% CO_3 , 1.54% HCO_3 , 0 Mg, and 3.13% insolubles. The reserves were estimated to be 0.67 million tons of Na_2SO_4 (Bernasconi and Cangioli, 1985). Garcia del Cura and Ordonez (1992) noted production by Sulfarentina SAMIC from the La Lobiera deposit in Santa Cruz. Also, development work was under way for the production of 30,000 t/yr of Na_2SO_4 from the 60-m deep brines of the Salar de Huyamampa in the Santiago del Estero province. The brine contained 6.5% Na_2SO_4 , 16% NaCl and had reserves for 30 yr of production.

Puna Region (Andes, NW Corner of Argentina)

About 6,000 t/yr of mirabilite have been produced from the Rio Grande Salar in Salta province (Garcia del Cura and Ordonez, 1992), and McIlveen and Cheek (1994)

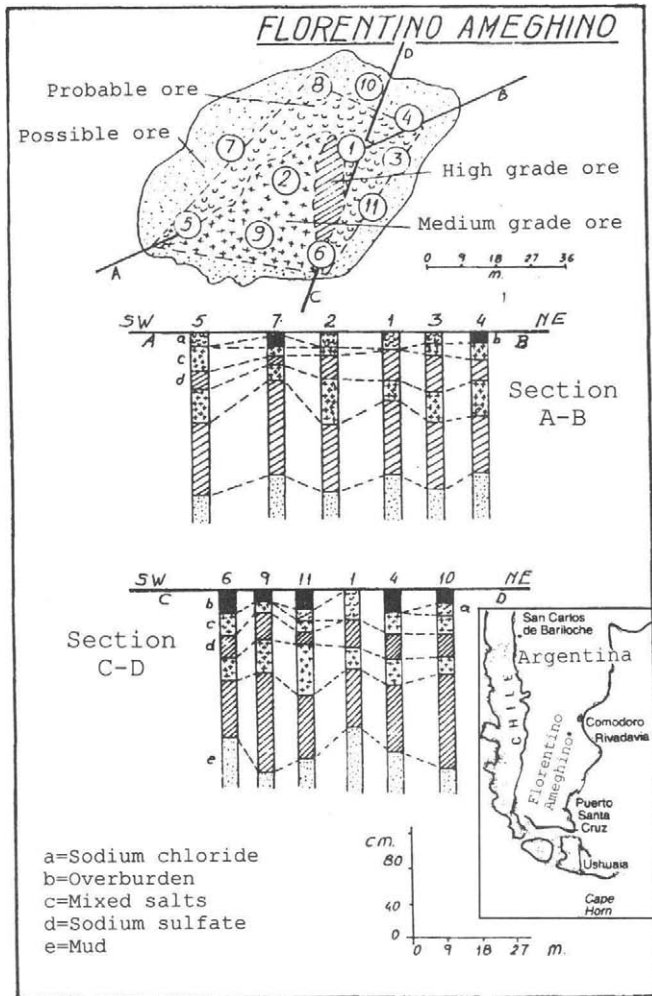


Figure 3.5 A typical commercial sodium sulfate playa in Santa Cruz province, Argentina. (From Bernasconi and Cangioli, 1985; by permission of the Asociación Geológica Argentina.)

noted a mirabilite deposit in Jujuy province with an area of 53 km² at an altitude of 3353 m. The mirabilite bed is 4.6 m thick in the center and tapers toward the edges. There is a thin crust of halite, thenardite, and gypsum on the surface of the playa, and brine below the surface. The total sodium sulfate production in Argentina was 32,000 t in 1986 (Nanni and Alurralde, 1988) and 11,000 t in 1990. A second production area was from the Aguas Blancas salar (near Oran, in Salta Province) with its glacial sediments (Cortelezzi and Solis, 1983; Cortelezzi, 1969).

CANADA

General

The 520,000 km² (200,000 mi²) Great Plains area of the southern part of central Canada, and northern North Dakota and Montana contains by far the greatest collection of sodium sulfate lakes and playas in the world. This prairie land stretches in an E–W direction 1600 km from near Winnipeg, Manitoba, to the Rocky Mountains in Alberta, and from the Precambrian Shield formation in the north into the United States. However, the majority of the larger sodium sulfate lakes in this zone are concentrated in a NW to SE band 160–480 km wide by 640 km long, as shown in Fig. 3.6. The area in which the deposits lie is generally flat to gently rolling, with occasional terraced valleys cut by glacial meltwater. The entire area has fairly recently been covered by glaciers, and much of the present surface was formed by the recession of the last period, the Wisconsin ice sheet 13,000–17,000 years ago. The glaciers left a thick mantle of glacial drift (average 46–61 m [150–200 ft] thick; maximum ~300 m), with a surface containing an estimated 5.5 million individual saline lake basins. Some were formed since the glaciers melted, and most of them have areas less than 100 km² and are <3 m deep when flooded in the spring. Their brines contain predominately sodium sulfate, with lesser amounts of magnesium sulfate, and much less sodium carbonate and sodium chloride. Only a few have major amounts of or principally contain magnesium sulfate, sodium carbonate, and/or sodium chloride. Of the lakes, perhaps 100 or so (70 in Saskatchewan; Last and Slezak, 1987) could be classified as potential sodium sulfate deposits (i.e., containing more than 100,000 t of sodium sulfate; Table 3.2), with the total reserves in all of the lakes being about 80 million mt of Na₂SO₄ (of which perhaps 30–40 mt might be commercially recoverable; Last, 1994; Cole, 1926).

Many of the sodium sulfate deposits appear to be in old pre-ice age valleys or river channels that are now covered, but have again formed modern depressions. Some of these lakes, such as Ingebrigt, were very deep with steep sides, apparently caused by sinkholes formed by the melting of large blocks of buried residual glacial ice. Beneath some of these lakes there are also extensive aquifers trapped in the glacial fill above the old valley floor (Rueffel, 1968). Others lakes are in more recently formed broad, flat depressions, and most of the basins have well-to-poorly sorted gravels and sands beneath and adjacent to them. In areas the glacial till appears to be somewhat classified, with the coarser, more recently formed alluvial sand and gravel on the surface. All of the lake bottoms are covered by a relatively thin layer of recent calcareous clay and silt, and on top of that there is black to dark green fine-grained sands, silts, clay, and organic matter. In some lakes this organic-rich layer also covers all or part of the mirabilite deposit. This near-surface mud usually contains sulfate-reducing bacteria that can generate prolific amounts of hydrogen sulfide.

The typical evaporation pattern for the playa lakes is to become at least partially covered by 5–50 cm of surface salts (with some silt and clay) by the end of summer.

a

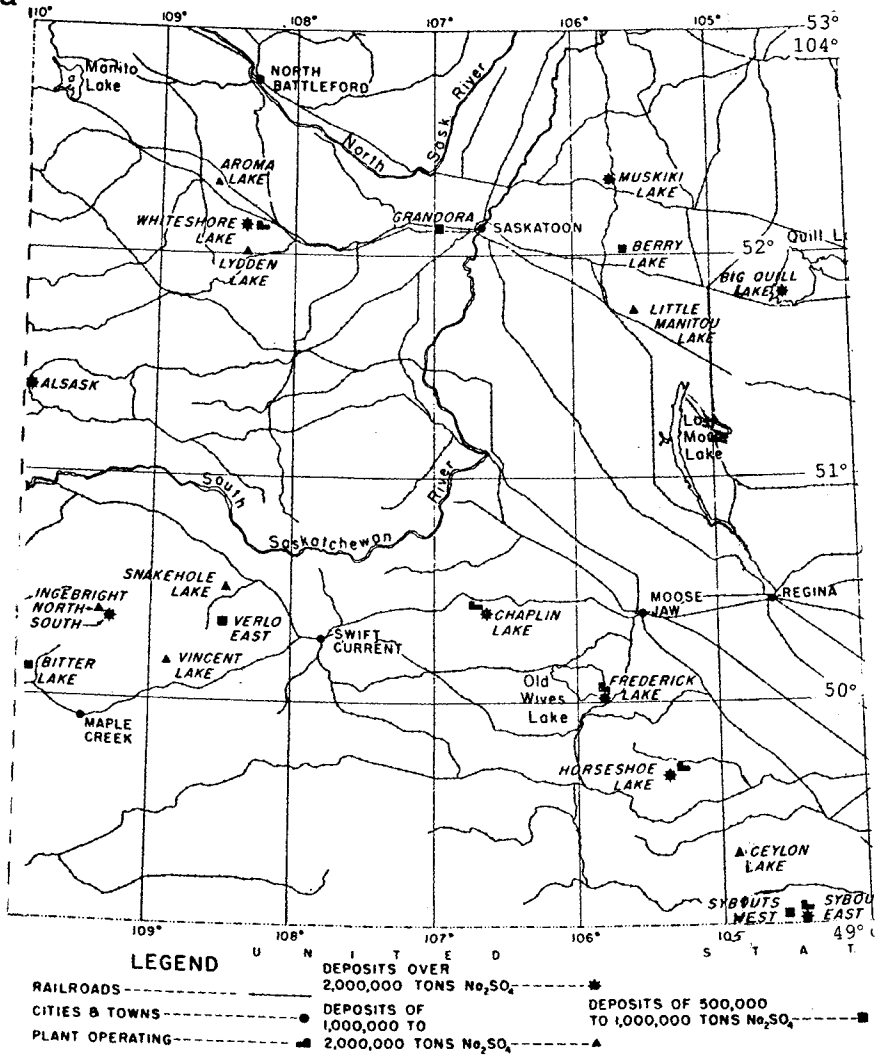


Figure 3.6 (a) Location of plants and major sodium sulfate lakes in Saskatchewan, Canada. (From Tomkins, 1954; by permission of the Saskatchewan Geological Survey.) (b) Some of the major sodium sulfate lakes in the Canadian–United States prairie area. (From Murphy, 1996; by permission of the North Dakota Geological Survey.)

In late summer and autumn, as crystallization from the remaining lake brine commences, a surface layer of fairly pure mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) forms, perhaps preceded by some thenardite (Na_2SO_4), and often followed by some later dehydration of mirabilite to thenardite. Some or all of these “intermittent” surface salts

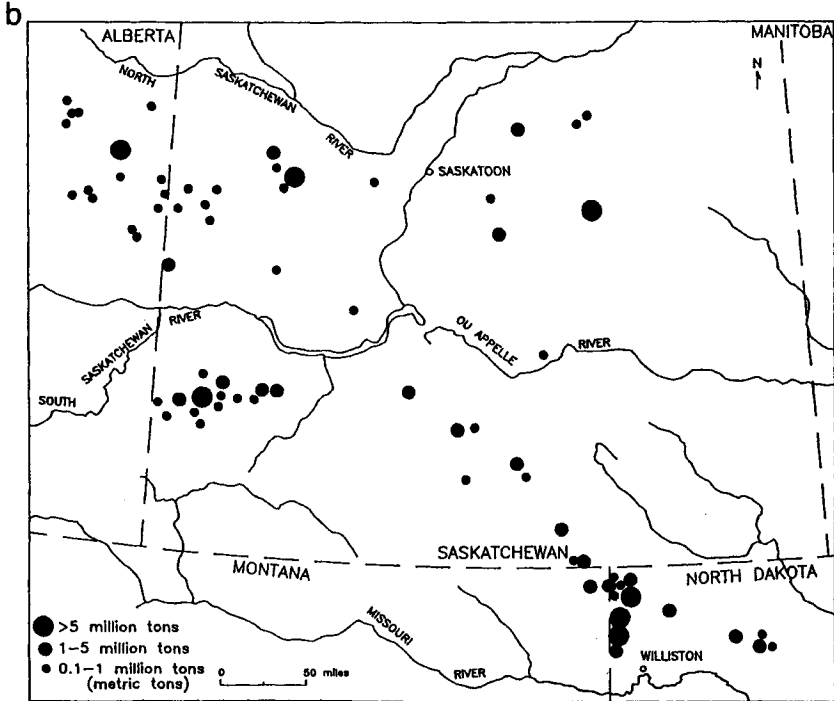


Figure 3.6 (continued)

dissolve again in the spring as the basins flood, but some may remain as a “permanent” salt body. The climate in the area is arid to semiarid, with warm summers (20°C mean in July), very cold winters (-17°C mean in January), and a considerable net annual evaporation rate (average 30 cm/yr precipitation, 125 cm/yr evaporation). These conditions appear to have been fairly constant for the last 3500 yr (Last and Slezak, 1987, 1988).

Sodium Sulfate Source

The larger sodium sulfate deposits are concentrated in the most arid sections of the Canadian prairie (and into Montana and North Dakota), with much of this area also having a very saline brown to dark-brown soil (an estimated 3600 km^2 [1390 mi^2] zone). The soil salts consist predominately of sodium sulfate with lesser amounts of magnesium sulfate. Gypsum, pyrite, and bentonite clay are all common minor constituents in the predominantly Cretaceous marine shale that underlies the glacial drift, as well as in the glacial till and boulder clay formed from this rock. Thus, the raw materials for sodium sulfate deposits were present in large quantities. Because

Table 3.2
Estimated Reserves in Some of the Major Canadian
Sodium Sulfate Lakes^a

Name	Tomkins (1954)	Cole (1926)
Big Quill Lake	11.0	7.0
Ingebright South	9.0	11.0
Whiteshore Lake	6.5	8.7
Horseshoe Lake	3.7	4.0
Sybouts East	3.3	3.9
Muskiki Lake	3.0	4.5
Chaplin Lake	3.0	—
Alsask	2.6	3.1
Frederick Lake	2.4	2.8
Metiskow Lake	—	2.3
Vincent Lake	2.0	2.5
Snakehole Lake	1.7	2.1
Little Manitou Lake	1.2	—
Ingebright North	1.1	1.2
Aroma Lake	1.1	—
Ceylon Lake	1.0	1.1
Verlo East	1.05	—
Lydden Lake	0.9	—
Sybouts West	0.8	1.1
Bitter Lake	0.8	—
Berry Lake	0.8	1.0
Grandora	0.6	0.5
Chain Lakes	0.35	0.13
Boot Lake	0.3	0.33
Richmond Lake	0.3	—
Eins Lake	0.25	—
Coral Lake	0.2	0.23
Akerlund Lake	0.2	—
Fusilier North	0.2	—
Horizon South	0.2	—
Neola Lake	0.15	—
Wiseton South	0.1	0.22
Regina Beach South	0.1	0.04

^aMillion mt; all in Saskatchewan except Metiskow.

of the permeable nature of much of the drift, some of the pyrite could be readily oxidized, allowing the resultant sulfuric acid to leach the surrounding rocks. Similarly, the gypsum in the till could be easily contacted and partially dissolved, followed by some calcium ion exchange of the resultant solution with the glacial clays to form sodium sulfate (see Chapter 1). Most of “the (larger sulfate) deposits are invariably located in areas where there is either glacial boulder clay or outwash (clay-forming) formations” (Edmunds, 1957). With such a large excess of clay compared

to the gypsum, most of the dissolved calcium becomes ion-exchanged or tied up as bicarbonate, leaving little gypsum in the typical ground- or springwater. Once formed, the sodium sulfate, along with the other normal rain or groundwater leachate minerals, can then accumulate in the adjacent drainage basins, or move to the surface soil by capillary action. Thus, sodium sulfate was usually the major salt present in the soil, springs, and lakes. Naturally many other ions would also be present with the sodium sulfate, and in some basins different rock compositions would have allowed magnesium sulfate, or even sodium chloride and/or sodium carbonate/bicarbonate, to be the major or important salts that were leached. Studies on the δD and $\delta^{18}O$ of lake water, springs feeding into the lakes, and adjacent wells confirm that they all contain fairly normal meteoric water for the area, with a small content (perhaps up to 14.5%) of glacial till porewater (Kelley and Holmden, 2000).

Selective Crystallization and Seepage

Even with these favorable conditions for sodium sulfate formation and accumulation, however, the remarkable number and high purity of the entire area's deposits could only occur because of the summer crystallization of thenardite, and the fall, winter, and early spring crystallization of mirabilite. The latter salt has a very low solubility (as does astrakanite, epsomite, and natron) in this very cold area and would selectively crystallize, leaving a brine very low in sodium sulfate and high in magnesium and sodium chloride to seep away through the relatively thin clay bottoms of the lakes for perhaps as much as 80% of the year. This would result in a continual net purification of the sodium sulfate (and to a lesser extent magnesium sulfate and/or sodium carbonate).

Deposits in Saskatchewan

The most detailed analysis of the sodium sulfate lakes in Saskatchewan was conducted by Cole (1926), who drilled 25 of the larger lakes and took many samples of their springwater, lake brine, surface salts, and bedded deposits. These results have been averaged in Table 3.3, and the reported magnesium, carbonate, or bicarbonates adjusted when necessary (compounds were reported [instead of ions] that were sometimes incapable of coexisting with each other). In general, his spring analyses indicated water that after evaporation could have formed the reported lake brine, and the lake brine was very compatible with the deposit analyses. This consistency again indicates that the springs and runoff were the source of the deposits. All of the lakes had springs flowing into them, usually as seepage along their edges, but some had flows directly into the lake. When sampling pipes could be inserted deeply into the lakes' springs, most of their analyses were similar to the springs at the edges, being fairly dilute and often nearly potable. All (as the seepage springs) were at low, near mean-average annual temperatures, and their fairly normal, low mineral content (average 3070 ppm) also indicated that they were derived from the leaching of near-surface rocks. Sodium sulfate was usually present in the

Table 3.3
Average Analyses of Saskatchewan Sodium Sulfate Springs, Brine, and Salts, wt% (Cole, 1926)^a

	Na ₂ SO ₄	MgSO ₄	NaCl	CaSO ₄	CO ₃ /HCO ₃	Insol.	TDS	Density
Alsask, brine	3.7	0.2	4.9	—	0.4 ³ , 0.3 ⁴	—	9.6	—
Deposit	88.1	0.4	1.3	0.4	0.5 ³ , 1.6 ⁴	7.7	—	—
Aroma, brine ¹¹	3.6	2.8	0.8	—	—	—	7.1	1.067
Berry, brine	13.1	5.9	0.2	—	0.04 ² , 0.14 ⁷	—	19.4	1.173
Deposit	87.1	3.1	0.8	4.1	0.5 ⁴	4.4	—	—
Big quill, brine ¹¹	2.0	2.6	0.7	—	—	—	5.3	1.049
Boot, spring ^{1,15}	1358	1101	166	0	582 ² , 314 ⁷	0	3542	0.998
Deposit	89.5	3.5	0.7	0.6	1.6 ⁵ , 0.5 ⁶	3.6	—	—
Ceylon, brine	5.0	2.6	0.5	0.02	0.07 ²	—	8.2	1.09
Deposit	80.2	1.1	0.1	1.0	0.9 ⁴ , 1.6 ⁸	15.1	—	—
Chain, spring ¹	1100	0	44	—	228 ⁵ , 260 ⁶	30 ¹⁰	1630	—
Spring ^{1,15}	570	291	15	0	22 ³ , 338 ² , 261 ⁷	0	1508	0.999
Brine	11.4	2.1	0.4	—	—	—	13.9	—
Brine ¹⁵	13.4	2.1	0.01	0.2	0.01 ³ , 0.10 ⁴	0	16.0	1.150
Deposit	87.4	3.1	—	2.2	1.3 ⁵	6.0	—	—
Chaplin, brine ¹¹	6.6	1.9	0.9	—	—	—	9.4	—
Corral, spring ^{1,15}	899	1083	556	0	58 ³ , 305 ² , 233 ⁷	0	3185	1.002
Brine ¹⁵	14.3	1.0	0.01	0.12	0.001 ³ , 0.06 ⁴	0	13.8	1.135
Deposit	86.0	1.1	0.4	—	1.5 ⁵ , 1.9 ⁶	9.3	—	—
Deadmoose, br. ¹⁴	1.9	0.9	1.2	0.1	0.1 ⁴	—	4.2	1.035
Frederick, spg. ¹	947	0	7	—	307 ⁵ , 226 ⁶	36 ³	1520	—
Deposit	85.1	6.7	0.6	3.2	—	4.4	—	—
Freefight, br. ¹⁴	4.1	5.1	1.0	0.1	1.2 ⁴	—	11.5	1.105
Grandora, spring ^{1,15}	309	168	125	16	430 ²	0	1058	1.000
Brine ¹⁵	6.2	0.3	0.7	0.07	0.01 ³ , 0.03 ⁴	0	7.3	1.066
Deposit	75.9	1.0	0.5	0.8	0.9 ⁴	20.9	—	—
Horseshoe, dep.	92.3	1.1	0.6	1.0	0.1 ³ , 0.7 ⁴	4.2	—	—

Ingebright 1, spg. ¹	1210	200	320	—	682 ² , 445 ^{3, 4, 7}	—	2790	1.002
Lake Spg. Na ₂ SO ₄	10.3	3.2	1.8	—	0.3 ⁴	—	15.6	1.120
Lake Spg. MgSO ₄	2.2	6.9	6.0	0.7	0.3 ^{2, 4}	—	16.1	1.136
Brine	2.2	1.6	1.0	—	0.1 ⁴	—	5.0	1.045
Deposit	78.3	3.2	1.8	3.9	0.8 ⁴	12.0	—	—
Ingebright 2, spg. ¹	3350	660	590	547 ²	579 ³ , 268 ⁴	—	5990	1.0045
Deposit	88.6	0.8	0.4	1.8	0.1 ³ , 0.7 ⁴	7.7	—	—
Little Manitou, br. ¹¹	0	8.0	4.2	—	2.9 ⁹	—	14.6	1.136
Lydden, brine ¹¹	10.1	3.0	0.3	—	—	—	13.3	1.127
Deposit ¹¹	93.6	2.7	—	1.5	—	2.2	—	—
Metiskow ¹⁵ , spg. ¹	940	650	495	—	275 ⁴	—	2360	—
Brine	11.2	0.8	1.5	—	12.2 ³	—	14.7	—
Deposit	79.6	0.3	0.5	0.2	2.3 ³ , 2.8 ⁴	14.3	—	—
Muskiki, well ¹	518	1130	34	510	203 ²	250 ¹⁰	2606	1.003
Big spring ¹	77	655	66	211	364 ²	—	1373	1.002
Brine	10.8	17.1	2.11	0.07 ³	0.14 ⁴	—	30.2	1.260
Crust, Na ₂ SO ₄	86.3	7.6	0.7	5.1	0.3 ⁴	0.8	—	—
Crust, MgSO ₄	33.1	61.4	3.2	0.8	0.3 ³ , 1.3 ⁴	0.3	—	—
Deposit	73.8	10.6	1.0	3.3	0.1 ³ , 0.6 ⁴	10.6	—	—
Product, 1926	94.6	0.5	3.1	1.2	0.3 ⁴	0.3	—	—
Regina Beach 1, dep.	86.4	2.2	0.6	3.8	1.1 ⁴	5.9	—	—
Snakehole, spg. ¹	802	129	85	—	228 ⁵ , 214 ⁶	24 ¹⁰	—	—
Brine, 7/22	11.2	2.0	0.7	0.3	—	—	14.2	1.095
Brine, 3/24	—	5.0	1.6	0.1	0.2 ⁴	0.3 ⁹	7.1	1.061
Deposit	76.1	5.1	1.0	2.7	2.9 ⁵ , 2.5 ⁶	9.7	—	—
Sybouts 1, brine	11.9	2.4	0.3	0.2	0.15 ²	—	15.0	1.139
Deposit	85.0	1.8	0.3	2.1	0.6 ⁴	10.2	—	—
Sybouts 2, spg. ¹	1170	146	—	—	1440 ⁷	—	2750	—
Brine	13.3	0.7	0.4	—	0.1 ⁷	—	7.69	1.066
Deposit	74.3	0.6	0.1	1.0	0.7 ⁴	23.3	—	—
VerloEast, brine ¹¹	10.2	1.1	0.2	—	—	—	11.5	1.11

(continues)

Table 3.3

(continued)

	Na ₂ SO ₄	MgSO ₄	NaCl	CaSO ₄	CO ₃ /HCO ₃	Insol.	TDS	Density
Vincent, spring ^{1,15}	1820	0	300	0	24 ³ , 720 ⁴ , 260 ² , 194 ⁷	0	3331	1.000
Brine	13.4	1.5	1.9	—	0.1 ⁵	—	16.9	—
Brine ¹⁵	9.4	0.8	0.9	0.1	0.01 ³ , 0.09 ⁴	0	11.3	1.1073
Deposit	86.1	1.9	0.8	0.7	1.3 ⁵ , 0.4 ⁶	8.8	—	—
Whiteshore, spg. ¹	3770	275	8	3	1140 ⁴	—	4910	—
Spring ^{1, 15}	276	0	378	0	16 ³ , 69 ² , 383 ⁷	0	1132	—
Brine	8.3	4.5	1.4	—	0.2 ⁴	—	14.4	1.135
Brine ¹⁵	3.4	3.4	1.3	0.2	0.01 ³ , 0.04 ⁴	0	8.4	1.0785
Deposit	76.7	8.8	0.8	4.0	0.8 ⁴	8.9	—	—
Wiseton, brine	8.0	20.0	1.0	—	—	—	29.0	—
Averages (Number of lakes; not including Ref. 15):								
Springs ¹ (7)	1760	267	189	—	629 ² , 415 ⁴	—	3070	—
Brine (12)	10.2	2.4	1.2	0.05	0.27 ²	—	13.3	1.131
Brine ¹¹ (9)	10.1	1.8	0.6	—	—	—	12.9	1.122
Brine ^{11,12} (5)	4.3	7.8	2.2	—	—	—	14.3	1.141
Crusts, Na ₂ SO ₄ (8)	97.1	1.3	0.6	0.2	0.4 ⁴	0.4	—	—
Crusts, MgSO ₄ (3)	60.2	30.6	3.1	4.3	0.8 ⁴	1.0	—	—
Deposits (18)	83.8	2.5	0.6	2.0	1.3 ⁵	9.8	—	—
Deposits ¹¹ (21) ¹³	80.0	4.4	0.5	3.8	—	11.3	—	—

^aKey to superscript numbers: 1, ppm; 2, Ca(HCO₃)₂; 3, Na₂CO₃; 4, NaHCO₃; 5, CaCO₃; 6, MgCO₃; 7, Mg(HCO₃)₂; 8, Al₂(SO₄)₂; 9, MgCl₂; 10, Al₂O₃, Fe₂O₃; 11, Tomkins (1954), Halburt (1999); 12, Winter; 13, 13 Na₂SO₄ lakes, 8 MgSO₄ lakes; 14, Last 1994; 15, Kelley and Holmden (2000).

springwater, along with many other ions. This included typical amounts of calcium, magnesium, and bicarbonate, causing calcite (and sometimes gypsum and dolomite or magnesite) to crystallize from this water as it evaporated. The springwater rapidly mixed with the lake brine, and when it cooled it sometimes formed mounds of salts in the winter, or "mud holes and chimneys" through the deposited mirabilite. However, a few of the lake springs did appear to have had a deeper origin, being warmer and more concentrated at depth, and in the winter formed even larger mounds of deposited mirabilite.

The brine from the lakes was usually sampled in midsummer, after the spring flooding of the lake and the surface salts had redissolved, but before evaporation (and/or evening cooling) had caused renewed crystallization. Thus, because of the leaching of the winter-crystallized mirabilite, a high sodium sulfate content was usually obtained. Later the brine would have less sodium sulfate because of the nearly complete crystallization of the mirabilite in the winter. As an example of the difference that the time of sampling made in the analyses, in Snakehole Lake in July the Na_2SO_4 content was 11.2%, whereas in March it was listed as zero (probably an error, since it should have been $\sim 1\%$). In July the MgSO_4 was 2.0%, and in March it was 5.1%; the corresponding values for NaCl were 0.7% and 1.6%, the total salts 14.2% and 7.1%, respectively, and 0.3% MgCl_2 in March.

The surface crust analyses is also highly variable, depending on the lake's brine analyses, the degree of crystallization, and the time of year. In most of the lakes with a fairly high sodium sulfate brine, the cool late summer and autumn evenings crystallize mirabilite before the other salts deposit with the daytime evaporation. As a consequence, the surface crust on these lakes contains quite pure sodium sulfate (97.2% average) with some-to-much thenardite from the daytime dehydration of the mirabilite (and in some lakes salting out by NaCl). The small magnesium sulfate content is probably present as astrakanite ($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$), and some of the sodium chloride as dissolved salts in the entrained brine. Three of Cole's (1926) lakes had a high magnesium sulfate content, giving an average of 30.6% MgSO_4 in the surface crust, with 3.1% NaCl. One of these lakes (Muskiki) had alternate layers of high MgSO_4 (61.4%) and high Na_2SO_4 (86.3%) in the surface crust, as the two salts crystallized successively from the brine (the astrakanite–epsomite [$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$] first by summer evaporation, and then the mirabilite by evening cooling). Only one lake (Senlac) had a high-NaCl brine and crystallized zones of fairly pure sodium chloride (which was once commercially harvested). In many of the high- Na_2SO_4 lakes some of the mirabilite surface crust has also been commercially harvested on a limited scale.

Most of the sodium sulfate lakes apparently do not contain an appreciable permanent bed of mirabilite–thenardite, although in Saskatchewan 19 of the 25 that Cole (1926) examined and 5 others that Tomkins (1954) reviewed do. Their deposits averaged 83.5% or 80.0% Na_2SO_4 , respectively, and only 2.5% MgSO_4 . The high- MgSO_4 lakes contained more magnesium sulfate in the mirabilite, such as Muskiki averaging 10.6%. Most of the deposits averaged 11–15% insolubles. The deposit

thickness varied from 0.6 to 40 m (2 to 130 ft; the normal range was 0.6–1.8 m), and the mirabilite content was 0.1–25 million tons (0.04–11 million t Na_2SO_4 , including values for the lakes that contained only brine). In all cases the mirabilite was interlayered with clay and calcium carbonate beds, sometimes also containing gypsum. The possible presence of sodium carbonate or bicarbonate salts in the deposits (or in the brine) was hard to determine from Cole's (1926) studies, since gypsum and magnesium sulfate were often reported with carbonates and bicarbonates, which is not possible.

Deposits in Alberta

With the sodium sulfate lakes in Alberta, much more understandable analytical data have been published, showing an interesting variation in the lakes' summer brine content (Table 3.4). Govett (1958) reported on 35 Alberta lakes, and of these 25 had a fairly high sodium sulfate content. Eight of the other lakes were sampled in June, and seven contained very dilute brine, making it uncertain whether the surface salts had not yet dissolved or their dilute water and the earlier sampling date was merely a coincidence. Eleven of the 25 high-sulfate lakes also had a fairly high carbonate/bicarbonate content, and two others had both high carbonate/bicarbonate and high chloride (and all, as would be expected because of precipitate formation, had almost no magnesium or calcium). It thus appears that the lakes in the northwest corner of the strong-sodium-sulfate area (in other words, Alberta) tend to be higher in carbonate–bicarbonate. Because of the steep solubility curve of natron

Table 3.4

Brine Analyses of Various Sodium Sulfate Lakes in Alberta, Canada, wt% (Govett, 1958)

	Area ^a	Na	Mg	K	Ca	SO ₄	Cl	CO ₃	HCO ₃	TDS	Density
Coates	190	4.8	1.0	—	0.04	14.8	0.8	—	0.3	21.7	1.191
Horseshoe ^b	640	9.5	0.2	—	—	8.2	0.9	6.9	—	25.7	1.212
Minburn ^b	25	3.1	0.2	—	0.01	7.0	0.1	—	0.1	10.5	—
Oliva-Carrier	449	2.6	—	—	—	5.0	0.1	2.3	0.5	10.5	1.103
Lake 13	320	5.7	0.2	—	—	11.1	1.0	0.2	0.5	18.7	1.166
Lake 26	500	5.7	0.01	—	—	6.7	0.4	2.2	1.2	16.2	1.150
Lakes 27, 28	510	5.7	0.01	—	—	9.2	0.3	1.1	0.4	16.6	1.155
Lakes 30, 31	360	2.4	0.01	—	—	4.2	0.1	0.4	0.2	7.3	1.061
Averages, high (number of lakes):											
CO ₃ (9)	325	4.4	0.1	—	—	6.6	0.4	1.9	0.4	13.9	1.128
CO ₃ +Cl (2)	590	3.1	0.02	—	—	3.7	1.9	0.5	0.3	9.5	1.075
Mg+Cl (4)	95	5.1	1.0	0.3	0.04	14.6	0.7	0.02	0.1	21.8	1.210
SO ₄ (8)	497	1.1	0.6	0.03	—	2.3	0.2	0.1	0.1	4.3	1.030

^aArea in acres.

^bCole (1926); Horseshoe Lake was called Metiskow Lake by Cole.

($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), it would also tend to crystallize in the fall, winter, and early spring, and thus slowly concentrate in the brine by selective seepage of the other salts.

Twelve of the lakes had a modest magnesium content (and almost no carbonate/bicarbonate) along with their much higher sodium sulfate, and thus appeared to be more similar to the majority of those in Saskatchewan. In eight of these the brine was fairly dilute (an average of 4.3% total solids). No drilling was done in this study to determine solid phase deposits (if any), so only Metiskow Lake that was drilled by Cole (1926; it was called *Horseshoe Lake* by Govett, 1958) was known to be a potential commercial deposit. It has the distinction of having the highest carbonate content (6.9%) in its brine of the Canadian lakes (according to Cole's analysis, or 12.2% Na_2CO_3 , along with 11.2% Na_2SO_4 , 0.8% MgSO_4 [?], and 1.5% NaCl). Cole also indicated that there was both sodium carbonate (2.32%) and bicarbonate (2.75%) in the deposited mirabilite salts, which could be trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot \text{H}_2\text{O}$) and nahcolite (NaHCO_3), but this is improbable in the area's cold climate.

Specific Deposits

The commercial recovery of sodium sulfate from the Canadian sodium sulfate lakes commenced in 1918 at Muskiki Lake near Saskatoon. Since then there has been continuous production, reaching a maximum in 1974 of 565,000 mt/yr, and more than 25 lakes have at one time been commercially operated (even though some of them were quite small). Perhaps 45 other lakes contain sufficient sodium sulfate to be considered as commercially recoverable under favorable circumstances. The estimated Na_2SO_4 reserves of the larger lakes are listed in Table 3.2, and in 1976 there were eight plants in Saskatchewan and one in Alberta producing sodium sulfate from the Canadian lakes (Fig. 3.6); at Alsask, Chaplin, Frederick, Horseshoe, Ingebright, Metiskow, Snakehole, Sybouts East, and Whiteshore). A few of these deposits will be briefly described below.

Chaplin Lake

Chaplin Lake is located 97 km west of Moose Jaw on the Canadian Pacific railway and the Trans-Canada Highway in a broad, shallow valley. The deposit has no permanent beds of mirabilite, but is thought to have some mirabilite disseminated in the clay under the lake, as well as sodium sulfate in the lake's brine (Halburt, 1999). Before the initial commercial operations were started, the brine often concentrated sufficiently in the summer to form a 36–61 cm layer of mirabilite in the deepest zones when it cooled and crystallized in the fall. The crystals sometimes covered up to a 40 km² area (the lake bed then had an area of 52 km²), making the total deposit appear to contain about 3 million tons of Na_2SO_4 . Most of the mirabilite in the surface crust dissolved in the spring, but sometimes a 15-cm semipermanent bed in the center could remain for several years. The lake could flood to a depth of 1.5 m during wetter periods, and in the summer occasionally dried up and created massive thenardite dust storms. After commercial operations started, the lake was

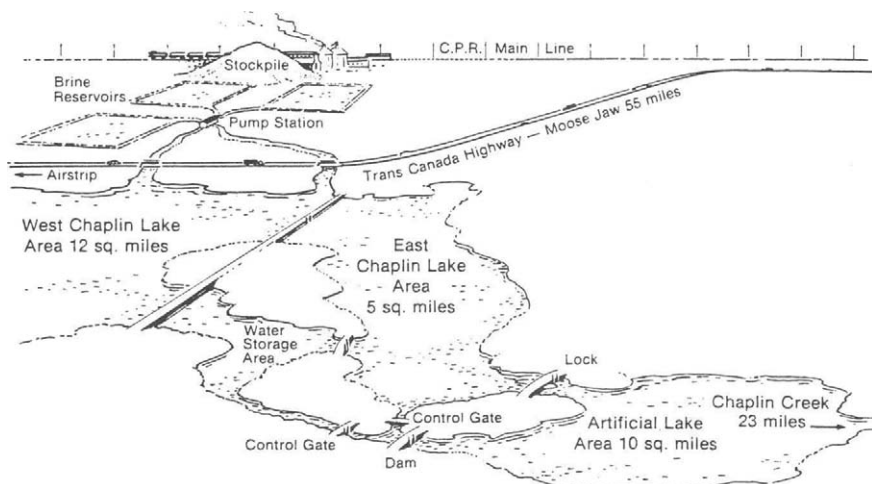


Figure 3.7 Chaplin Lake as modified for commercial production. (From Rueffel, 1976; courtesy of the National Research Council of Canada.)

divided into two sections in 1948 to better control the brine density, and an adjacent freshwater feeder lake was constructed (Fig. 3.7; Tomkins, 1954; Holland, 1949).

Several other Canadian lakes without large permanent mirabilite beds also appear to have the equivalent of more than 1 million tons of sodium sulfate in their brines, such as *Big Quill Lake* (7–11 million t), *Deadmoose Lake* (~1.6 million t), and *Freeflight Lake* (~1.3 million t). The latter two (Fig. 3.8) are deep, stratified,

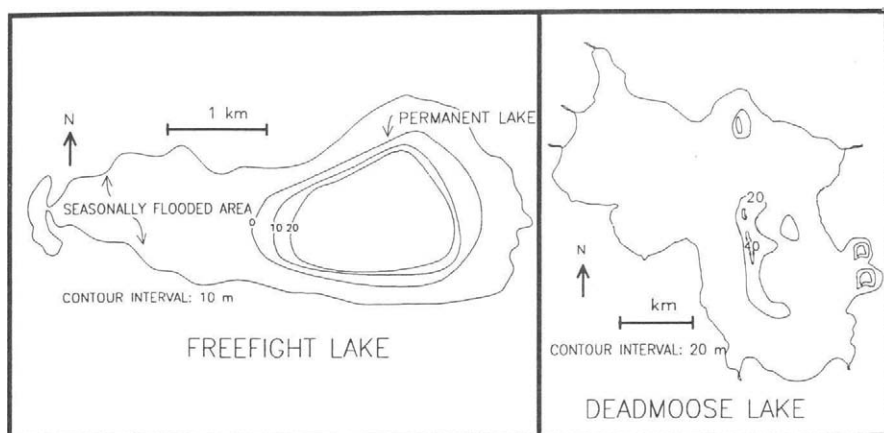


Figure 3.8 Freeflight and Deadmoose lakes. (From Last, 1994; by permission of the Society for Sedimentary Geology.)

permanent lakes with sodium sulfate contents of 3 and 11%, respectively, and which appear to be slowly forming beds of mirabilite (with some astrakanite [$\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$]) on their bottoms (Last, 1994; Last and Slezak, 1988).

Ingebright Lake, South

Ingebright Lake (Fig. 3.9) is the largest commercial sodium sulfate deposit in Canada, with 1954 reserves of 11 million tons of Na_2SO_4 (9 mil.t, Tomkins, 1954; 8 mil.t, Rueffel, 1968). Its area is about 280 hectares (700 ac; 340 ha or 840 ac, 0.8×3.6 km, Rueffel, 1968) and it lies about 21 m below the average level of the surrounding land (Cole, 1926). Summer temperatures in the area can reach 38°C , and in the winter -40°C (Rueffel, 1968). In the summer the lake is covered with an average ~ 25 cm brine layer, which forms a 5- to 30-cm surface salt crust. Its 275 ha (283 ha, Rueffel, 1968) salt deposit averages 6.7m (22 ft) in thickness. All of the mirabilite is compact and friable, and in the northern part of the lake it contains numerous clay layers (mostly thin, but 0.7–1 m thick at the 7.6–9.1 m level) and some clay in the crystals. In the south there is much less mud with the ore, and it is harder. Two zones in the lake have a thickness of more than 30 m (one is 42 m thick), and the purity slightly improves with depth.

The lake's drainage area is not large, and no streams flow into it. However, it has numerous seepages and springs around its perimeter, including five large springs that flow steadily throughout the year with a dilute, high-sulfate, medium carbonate/bicarbonate water (average 2800 ppm total salts). There are also many springs welling up through the crystal bed, being cold (7°C) and dilute in the north, and warm (15 – 18°C) and more concentrated in the south. The latter high-sodium-sulfate springs (Table 3.3) are capable of forming large mounds of quite pure mirabilite (98.4% Na_2SO_4 , 0.7% MgSO_4) in cold winters, up to 3 m tall and 6.1 m (20ft) in diameter. The deposits from the brine springs have also raised the top of the crystal bed in the south by about 0.46 m, causing there to be a greater springtime brine depth in the north, which may not completely evaporate in the summer. The northern freshwater springs appear to well up through "pipes" or "chimneys" of mud, since they are dilute enough to dissolve any overlying salts (Cole, 1926). Rueffel (1976) noted that in the spring the average brine depth on the lake is 0.3–0.6 m, the average precipitation in the area is 23 cm/yr, and the average (water) evaporation rate is 91 cm/yr.

Metiskow Lake

Metiskow Lake (Figs. 3.10, 4.11) is located 11 km southwest of the town of Metiskow in southeastern Alberta. Its area is 165 ha, it is about 3.2 km long, and narrow areas somewhat divide it into four sections. The mirabilite beds are up to 9 m thick in the north and 17 m thick in the south. The total reserves are about 3.5 million tons of Na_2SO_4 , and insolubles make up 15–50% of the ore (including the interlayers of mud). The lake often becomes completely dry in the summer and floods to >0.6 m brine depth in the spring. There are many small springs around

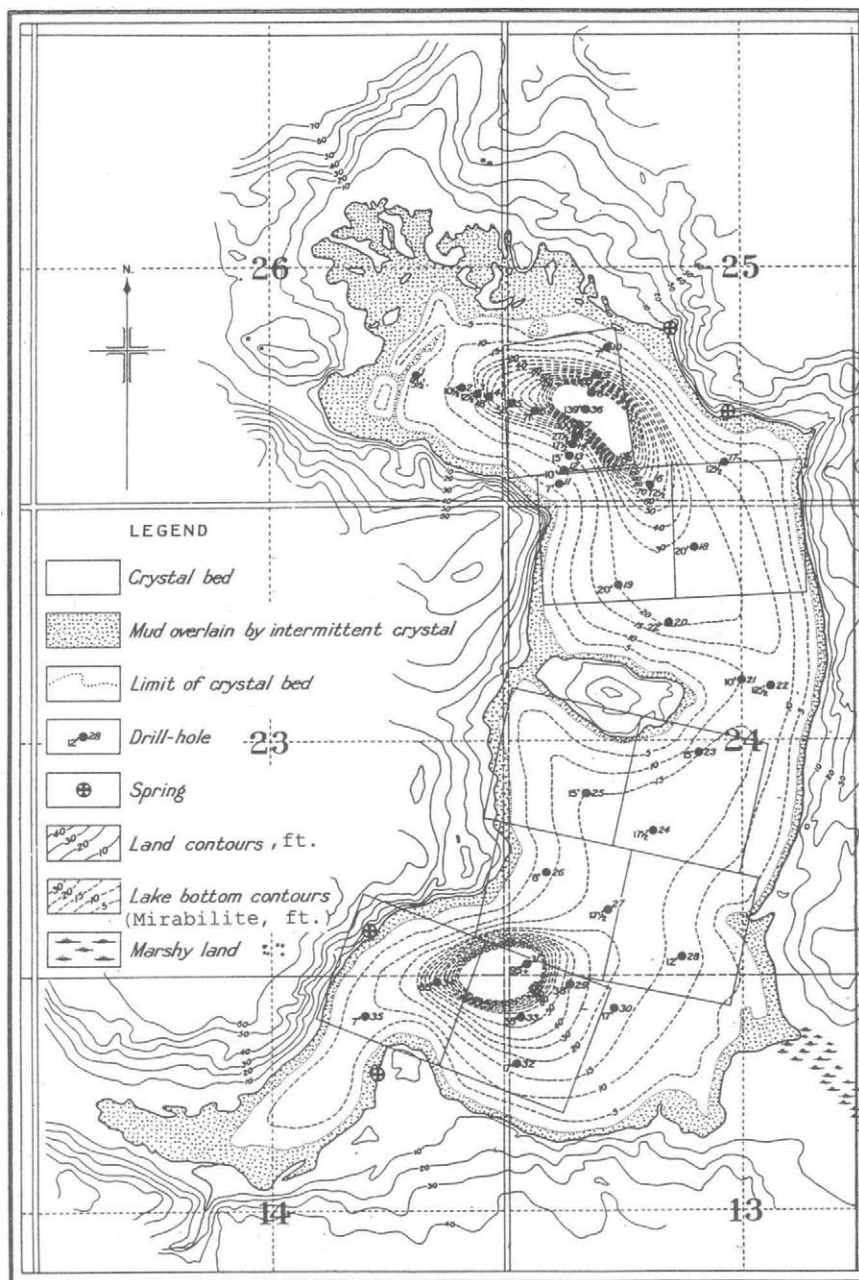


Figure 3.9 Ingebright Lake, Saskatchewan. (From Cole, 1926; by permission of Natural Resources Canada.)

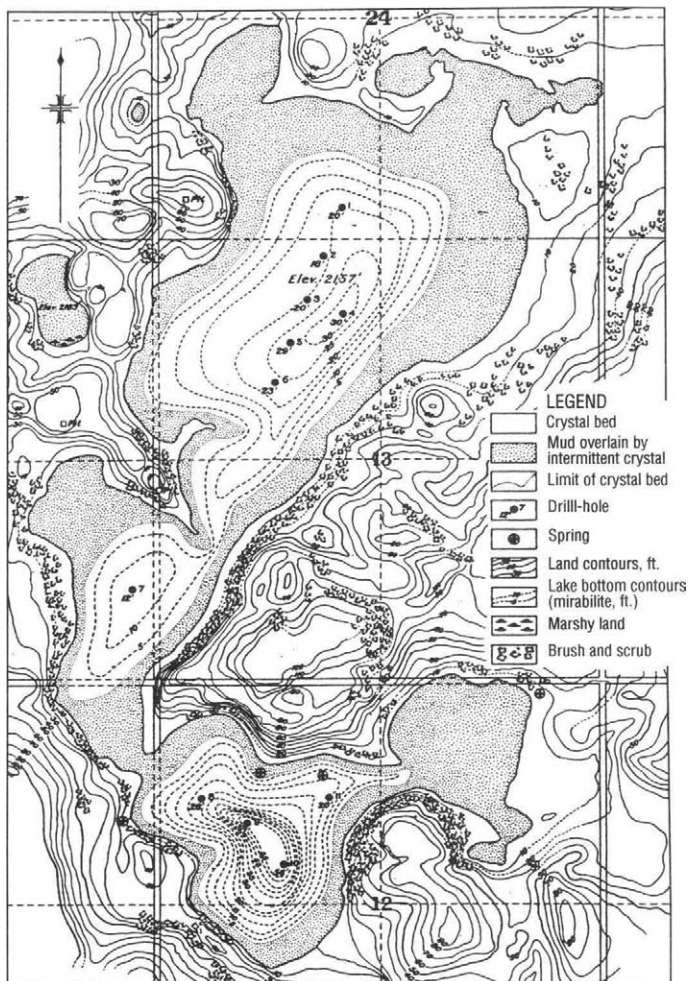


Figure 3.10 Metiskow Lake, Alberta. (From Cole, 1926; by permission of National Resources Canada.)

the lake shores, and several intermittent streams entering the lake (MacWilliams and Reynolds, 1973). The lake occupies the lowest portion (657 m elevation) of a large drainage basin that is hilly and wooded. Most of the lake's banks are steep and 18–37 m high, except for a broad valley to the northeast. Some of the deeper mirabilite and mud layers are very hard (Cole, 1926).

Sybouts Lake, East

Sybouts Lake (Fig. 3.11) is located near Gladmar, Saskatchewan, which is just across the U.S. border from Plentywood, Montana. It is typical of many of the

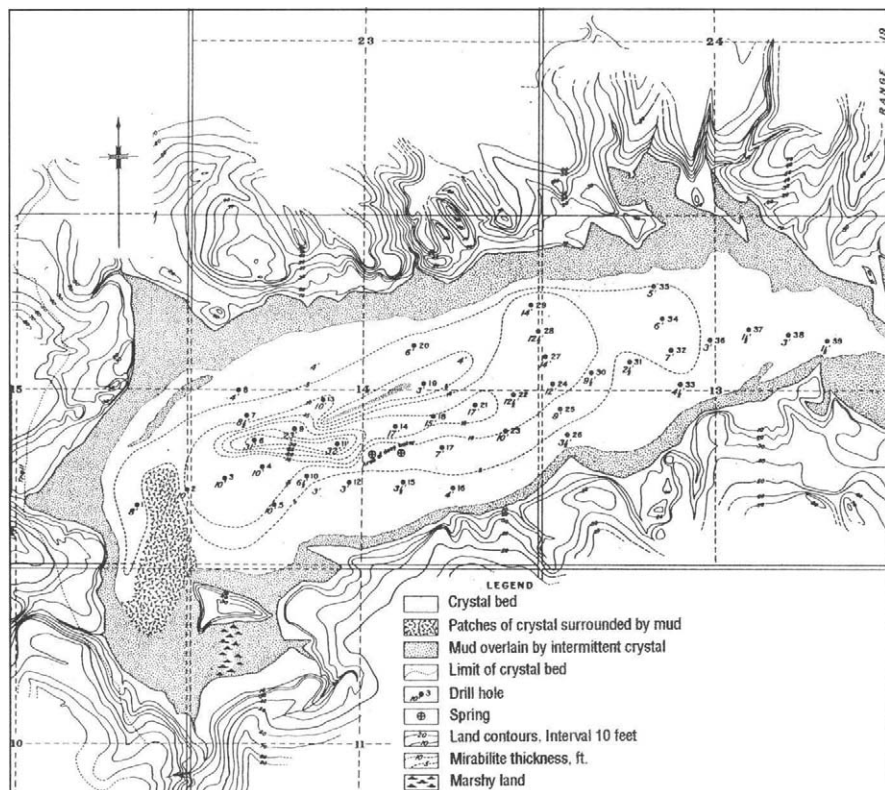


Figure 3.11 Sybouts Lake, Saskatchewan. (From Cole, 1926; by permission of National Resources Canada.)

Canadian sodium sulfate lakes in occupying a closed basin in boulder clay knolls, in this case forming steep 12 to 2-4 m banks for most of its periphery. The surrounding area is stony and gravelly, with large rounded pebbles and rocks, and in places the lake surface is covered with gravel instead of mud. The lake is >4.8 km long (E-W) and 910–1200 m wide, giving it an area of 255 ha (630 ac). Most of the numerous springs in this lake are under the crystal body, with more in the western half of the deposit. They appear to be brine springs since small cones are formed at most of their orifices, but one has formed a mound 1.8–2.4 m high and 300 m in diameter. Two large freshwater springs have formed brine pools that are more than 0.6 m deeper than the rest of the lake in the summer. The summer brine contains quite pure sodium sulfate, and the permanent mirabilite bed is thicker in the western end (up to 9.8 m) than in the east (up to 3.7 m). The deposit is free of mud on the surface, and hard and compact throughout its depth. In a few places near the edge the crystal is interlayered with mud up to 0.4–1 m thick, but most of

the mirabilite is free from mud layers. The insolubles in the deposit appear to be primarily those minerals that precipitate during the summer evaporation period (Cole, 1926). There has been large-scale commercial sodium sulfate production from the lake, and during 1941–1985 850,000 mt of Na_2SO_4 were produced (Murphy, 1996).

Whiteshore Lake

Whiteshore Lake is the second largest Canadian sodium sulfate deposit, with reserves of 6.5 million t of Na_2SO_4 (8.7, Cole, 1926). The Lake lies in a narrow valley and is 17 km long in an E–W direction, has an average width of 0.8 km, an area of 753 ha (1860 ac) and low, shelving to steeply rising 3- to 4.6-m banks. The deposit occurs in only parts of the lake, with a large bed in the eastern half, and a series of smaller beds in the western end. Several fresh-to-dilute springs (the two largest flowed at 5–10 and 100–150 gpm and contained 520 and 4580 ppm of SO_4 , respectively) occur in the margins of the lake, primarily on the southern shore of the eastern end, and there are a few in the east crystal body as large mud basins, 3–24 m in diameter. There are also high-sulfate (3.3% Na_2SO_4) brine springs throughout the crystal bodies that result in some small mound formation, and in general cause the mirabilite to be thickest in their areas. The summer brine is quite rich in sodium sulfate, forming very pure surface crusts. The large eastern deposit is about 8 km long by 0.4–0.8 km wide, averaging 0.9–2.1 m in thickness (with areas up to 3–4.3 m). It is composed of soft and muddy crystals for the top 1.5 m, but below that the mirabilite is harder and clearer. In all areas it is surprisingly impure (76.7% Na_2SO_4 , 8.8% MgSO_4 , and >12.9% insolubles) compared to the rather pure spring brine flowing into the lake. This indicates that the springs were not the main sodium sulfate supply for the deposit (Cole, 1926).

There are many other articles on the Canadian sodium sulfate deposits, such as by Slezak (1989), Slezak and Last (1985), Broughton (1984, 1976), Egan (1984), and Grossman (1968).

British Columbia

The *Fraser* (also called the *Cariboo* or *Green Timber*) Plateau of British Columbia (southwestern Canada) also contains a large number of alkali lakes occurring in glacial drift (Fig. 3.12). These lakes are generally similar to those of the Prairie provinces, but because of their mountainous location are more varied in composition, like those just to the south in Washington and Oregon in the United States. They, too, have tended to concentrate and purify the high-hydrate, low-winter-solubility salts, but in this case sodium carbonate is the dominant type. There are only a few lakes that contain primarily (or even major amounts of) sodium sulfate, and even fewer high-magnesium-sulfate lakes. The source of the salts appears to be hot springs with carbonates and bicarbonates, and the leaching of the surrounding rocks (including some gypsum) to give a mixed salt solution that concentrated in the area's arid climate. The high hydrate salts then preferentially crystallized (as in the prairies),

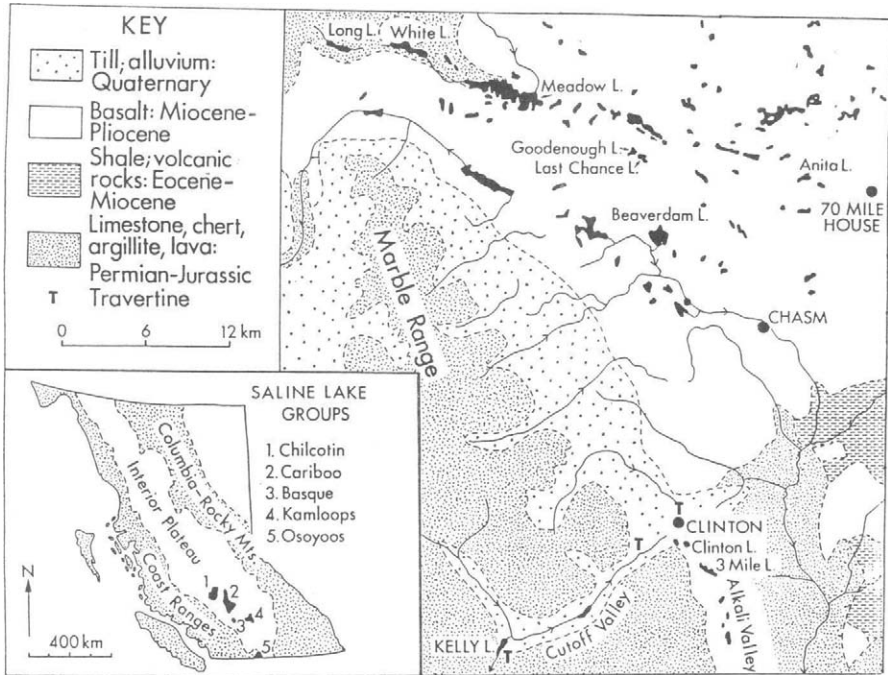


Figure 3.12 Map of the British Columbia saline lake area. Black areas are saline lakes. (From Renault, 1989; courtesy of Kluwer Academic Publishers.)

and the other salts seeped away to form the high-sodium carbonate, -sodium sulfate, or -magnesium sulfate lakes.

The planar-to-gently undulating intermountain Fraser Plateau is up to 75 km wide, at an altitude of 1050–1250 m, and has a surface of >5-m-thick glacial till or fluvioglacial deposits that vary somewhat in rock type throughout the plateau. The area's precipitation is 30–40 cm/yr (10–15 cm as snow), the evaporation rate slightly greater, the mean July daytime temperature 15°C (at night <5°C), and the mean January temperature –10°C. There are more than 750 lakes in the area, varying from fresh to highly saline. Most of the lakes are very small and contain water throughout the summer, but reduce their area by more than 50% (producing wide salt-crusted mud flats), and a few become totally dry. Many of the larger lakes, like some in Washington–Oregon, have a “spotted” bottom structure consisting of many round crystalline zones (Renault, 1989). Only a few of the lakes contain bedded mirabilite, and none have extensive sodium sulfate reserves (including in the brine). For example, Lake No. 2 is 3 ha in size, has mirabilite 2.1–5.9 m thick, but contains only about 80,000 t of Na_2SO_4 (Cummings, 1940). Various entering water, spring, brine, and salts analyses for the area are listed in Table 3.5.

Table 3.5
Analysis of Various High-Sodium-Sulfate Fraser Plateau
Waters, Brine, and Salts (ppm) (Renaut, 1987)^a

	Na	Mg	K	Ca	SO ₄	HCO ₃	CO ₃	Cl	SiO ₂
Rivers ^b	5.5	14	1.4	49	21	206	0	3.3	4.6
3 Mile Spr.	5670	9845	450	120	44,500	270	0	1350	0
Br.	3840	7310	320	265	36,490	0	0	395	51
Clinton Cre.	51	102	2.4	62	18	760	0	8.6	4.8
Spr.	136	538	24	3.8	1235	1090	255	7.9	6.5
Br.	21,800	61,500	1750	45	275,000	4500	0	3550	10
Last Chance Spr.	250	76	15	11	180	800	0	34	5.0
Br.	55,770	46	683	6.3	20,230	17,980	45,870	9790	29

Solid Deposits in the Kumloops Area (wt%) (Cummings, 1940)

	Na ₂ SO ₄	Na ₂ CO ₃	MgSO ₄	NaCl	CaSO ₄	Insol.
Lake No. 1, Crust	39.8	57.9	—	—	—	1.1
Lake No. 2, Crust	99.2	—	—	0.5	—	0.2
Bed to 1.2 m	83.8	—	2.7	—	—	13.5
Lake No. 3, Crust	48.6	1.9	19.8	2.5 ^c	2.7	21.6
Lake No. 4, Bed	32.8	1.4	62.0	1.6	2.1	—
Basque Lake, Bed	26.6	2.0 ^c	69.8	0.12	1.46 ^d	—
Inks Lake, Bed	60.0	3.0	31.7	1.5	3.7	—
Iron Mask Lake, Cr.	94.2	0.5	5.1	—	—	0.2
Bed	35.8	2.0	61.8	0.4	0	—

^aBr. means brine, Spr. means spring, Cre. means creek, Cr. means crust.

^bAverage of Porcupine, Cutoff Valley, 57 Mile Creeks, and stream "ML."

^cMgCO₃.

^dKCl.

CHILE

Chile has a large number of sodium-sulfate-containing lakes and playas (called "salars"; there are >100, mostly in northern Chile; Fig. 3.13), and a few of them have periodically produced a combined total of about 10,000 mt/yr of sodium sulfate. For instance, various salars near Iquique and at *Aguas Blancas* (95 km east of Antofagasta) have been mined for their mirabilite–thenardite (Na₂SO₄ · 10H₂O–Na₂SO₄) content. In the latter playa during the 1930s, ore was dried on the surface to form a partially dehydrated 85% Na₂SO₄ salt that was sold as an impure product. Another operation was at the *Salar de Pintados* in the Central Valley of northern Chile, near the town of La Guaica. In a >3 km² northeastern area it has discontinuous lenticular layers up to 40 cm thick of ice-clear, large mirabilite crystals. The altitude of the salar is 1000 m, and the area's average rainfall is less than 1 mm/yr. The

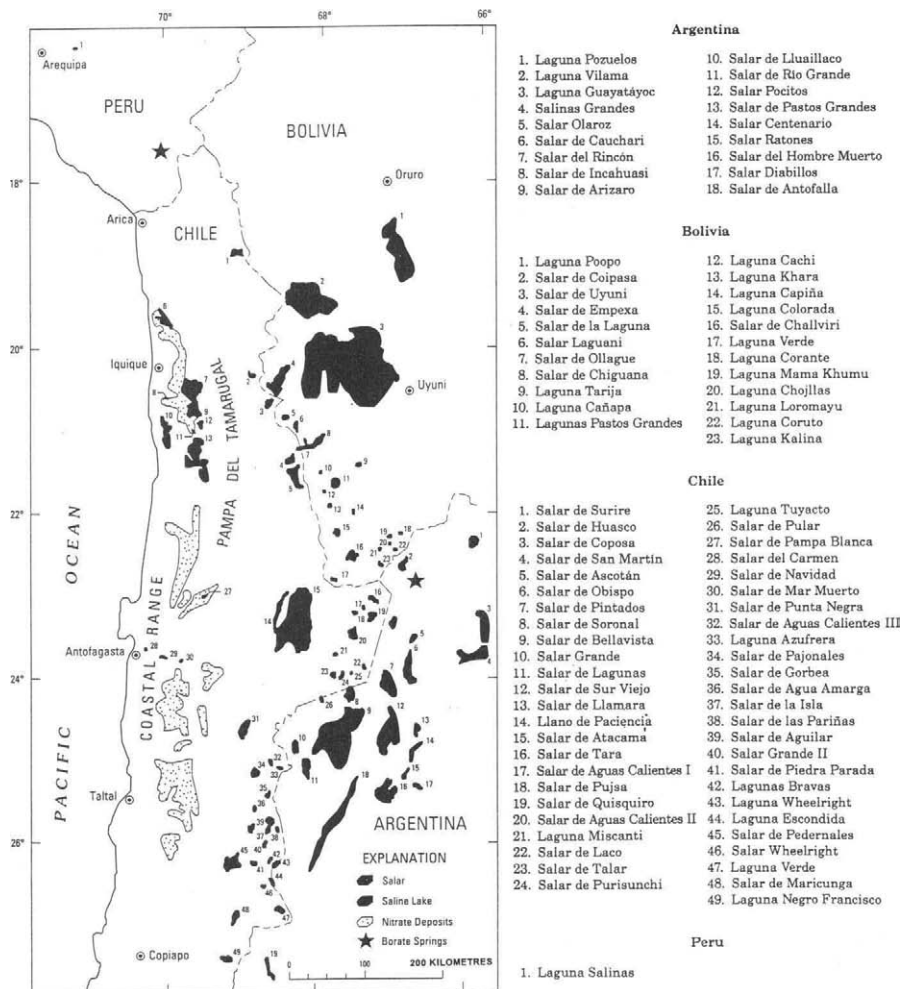


Figure 3.13 Location map for some of the salars in the central Andean Region. (From Ericksen, 1995; courtesy of the Geological Association of Canada.)

mirabilite rests on water-saturated mud containing a little gypsum and is covered by 20–30 cm of porous, granular white thenardite (some crystals are up to 20 cm long) accompanied by small amounts of halite (NaCl). Over the thenardite is 30–75 cm of broken, rough halite containing considerable clay and some thenardite. A small amount of hydroglauberite ($5\text{Na}_2\text{SO}_4 \cdot 3\text{CaSO}_4 \cdot 6\text{H}_2\text{O}$) has also been found with the mirabilite. Limited mining of this mirabilite–thenardite deposit has been conducted since the 1920s, as well as from the adjacent (to the south) *Salar de Bellavista* (Ericksen, 1995, 1963; Ericksen *et al.*, 1970).

Many other salars in Chile also contain brines with a high sodium sulfate content, such as the *Salar de Puja*, with (as 1000 g/liter): 28.1 SO₄, 27.7 Cl, 0.675 B, 28.5 Na, 1.30 K, 0.653 Mg, 0.375 Ca, and 0.137 Li (Garrett, 1998). The gigantic *Salar de Atacama* that is now being commercially operated for potash, lithium, and borax also has the potential to produce sodium sulfate from its brines (Goeler and Wilkes, 1991; Fueyo, 1989). However, since the operating company, Soquimich, also produces sodium sulfate from its sodium nitrate (caliche) operations, it would probably produce potassium sulfate from the Salar de Atacama instead. Many other articles have been written about the salars and/or the potential for sodium sulfate production in Chile, such as by Vila (1975) and Pena (1933).

CHINA

There are a large number of lakes, playas, and aquifer formations in China that contain high-sodium-sulfate brines or mirabilite (Na₂SO₄ · 10H₂O) deposits, and small-scale sodium sulfate production is obtained from many of them. Typical of the playa/lakes are those in the Qaidam Basin, Qinghai province (Fig. 3.14), such as *Da Chaidan Salt Lake*. A large potash (KCl) project was planned for this playa in 1999, with sodium sulfate to be produced later. It has a 130 km² saline surface and a brine-filled halite area of 30 km² that is >20 m deep with a 15% salt porosity. The lake's altitude is 3140 m, the area's evaporation rate 50 times the 80 mm/yr precipitation; the brine is always within 1 m of the surface, and 10 different sulfate minerals have been found in the playa. Mirabilite crystallizes prolifically from the

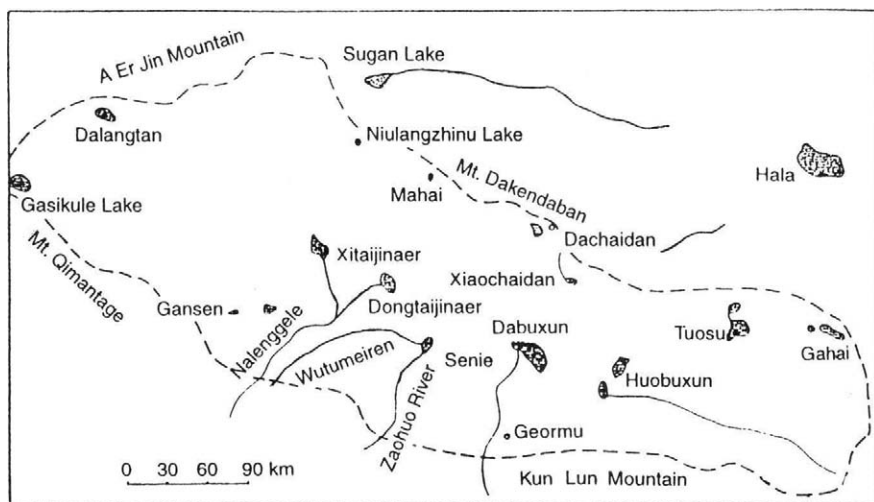


Figure 3.14 Saline lakes in the Qaidam Basin, Qinghai, China. (From Qian and Xuan, 1983; by permission of the Salt Institute.)

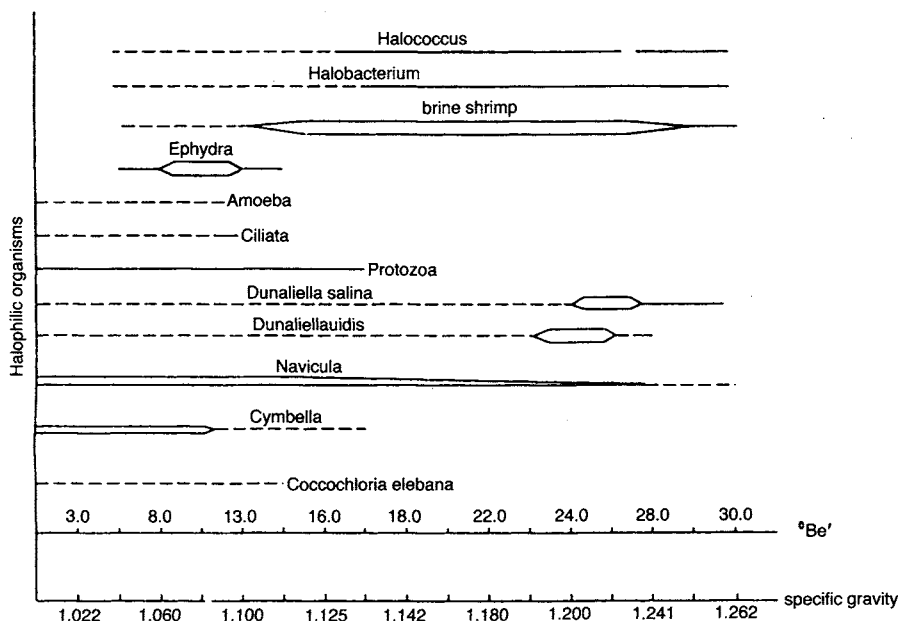


Figure 3.15 The life span of halophilic organisms as a function of brine density in Barkol Lake, China. (From Dongyan *et al.*, 1994, by permission of VSP International Science Publishers.)

brine when cooled, and the tentative sodium sulfate recovery process is based on crystallizing it in special ponds during the winter, and then solar evaporating the remaining brine to recover potash, boric acid, and lithium (Gao *et al.*, 1993). Many other articles have also been written on the Qaidam Basin, such as by Yang (1996), Vengosh *et al.* (1995), and Wang *et al.* (1992).

Barkol Lake in eastern Xinjiang province contains a large solid phase mirabilite deposit as well as a 215–338 g/liter brine. An interesting study of the biological organisms that live in this highly saline lake has been made (Fig. 3.15) by Dongyan *et al.* (1994), and Wei (1992). Li *et al.* (1992) studied its biomarkers. Also in Xinjiang province, *Lake Balikun* has a large mirabilite deposit that is commercially recovered. Experiments have been made with the solar evaporation–dehydration of the mirabilite to produce a commercial product (Ma *et al.*, 1998). In Xizang province there are a number of lakes with major mirabilite deposits, such as *Bange*, *Dong Cuo*, *Guojialin*, and *Ybu Cuo*, as well as in *Zhacang Chaka*, Tibet (Fig. 3.16; Chen, 1986; Yang and Zheng, 1985). Other deposits occur in the Henghang Basin (Long and Wang, 1994), and at Lixian, Hunan province (Qu, 1989).

A different type of deposit, with a high-sodium-sulfate aquifer brine, occurs 10–15 km west of Pengshan city, Szechuan province, on the western bank of the Minkiang River. The brine occurs at a depth of 18–50 m primarily in a band about 20 km long and 1–6 km wide that is roughly parallel to the river, with a second

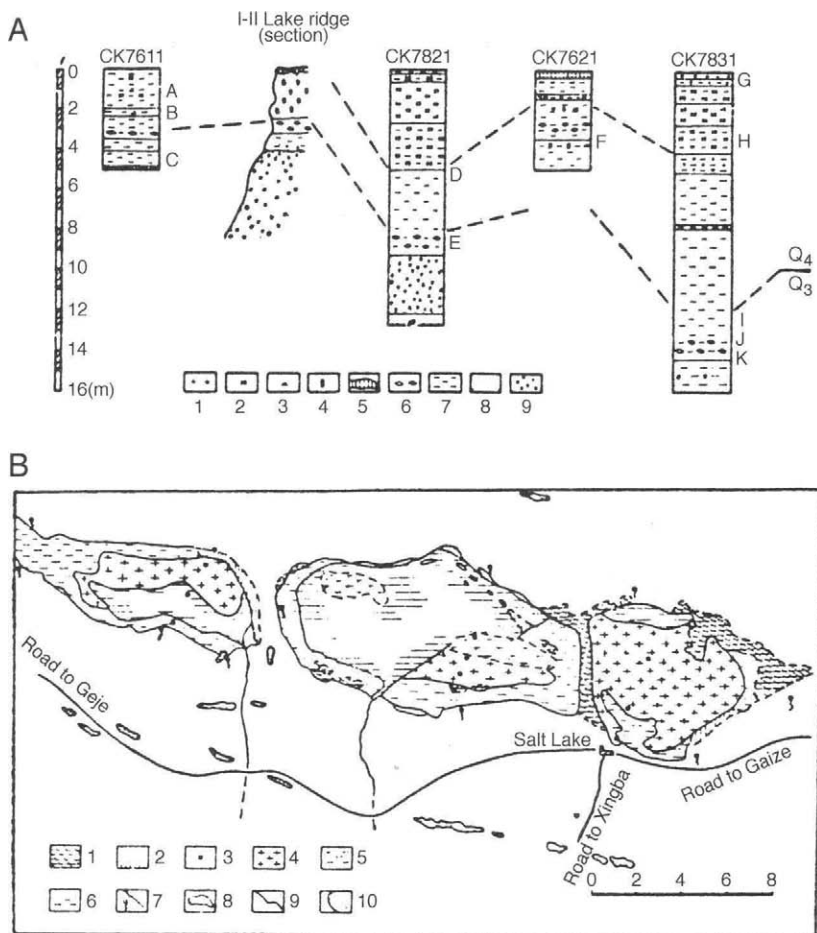


Figure 3.16 (A) A correlation for salt deposits in Zhacang Chaka Lake. 1, halite; 2, mirabilite; 3, gypsum; 4, kurnakovite; 5, pinnoite; 6, carbonate; 7, clay; 8, sand; 9, gravel. A, 5600 ± 150 yr; B, 8000 ± 130 yr; C, 10900 ± 200 yr; D, 9060 ± 120 yr; E, 15600 ± 600 yr; F, 7000 ± 110 yr; G, 1400 ± 690 yr; H, 4780 ± 180 yr; I, $13,400 \pm 160$ yr; J, $15,400 \pm 160$ yr; K, $20,000 \pm 350$ yr. (B) The distribution of the salt deposits in Zhacang Chaka Lake. 1, kurnakovite; 2, pinnoite; 3, position of drill hole; 4, halite; 5, mirabilite; 6, clay; 7, spring and river; 8, sinter terrace; 9, road; 10, lake water. (From Yang and Zheng, 1985.)

small band 0.5×2 km in size just north of the city. The brine is pumped from literally hundreds of wells into solar evaporation ponds, where mirabilite is crystallized in the winter and then dehydrated to form an anhydrous product. The brine occurs in the upper part of a 110-m-thick bed of Cretaceous and Middle Triassic green and yellow porous (with very small pores) limy clay that contains numerous

Table 3.6
Brine and Salts Composition of the Chaganor
Soda Ash Deposit (wt%)

Bed	Average thickness (m)	Na ₂ SO ₄	Na ₂ CO ₃ + NaHCO ₃	NaCl	KCl	H ₂ O	Insol.
1, Ore	1.39	11.90	26.10	1.38	—	56.86	3.22
Brine	—	2.27	6.30	14.86	0.33	—	—
2, Ore	2.44	11.13	27.34	1.21	—	56.46	3.51
Brine	—	2.11	6.39	13.80	0.41	—	—
3, Ore	2.46	10.00	28.91	1.19	—	55.53	3.77
Brine	—	2.30	6.08	16.17	0.58	—	—

Data from Zhang, 1998.

crystals of anhydrite. The brine averages, as g/liter, 97.8 Na₂SO₄, 8.9 NaCl, and 2.5 MgSO₄, with a density of 1.09 (9.19°Be) and reserves of 4.65 million tons of sodium sulfate (Hou and Yang, 1938).

By-product sodium sulfate is produced from a salt operation adjacent to a lake in Yuncheng, north of the Zhongtiao Mountains in Shanxi province. Salt has been recovered from this lake for centuries, and in 1986 it was reported to be producing 16,000 mt/yr of Na₂SO₄ (as well as by-product calcium chloride, borax, bromine, and iodine; McIlveen and Cheek, 1994). Sodium sulfate also occurs with several of the country's large soda ash deposits, such as at Chaganor. This Pleistocene deposit is located in the central part of the Inner Mongolia Autonomous region, 80 km southeast of Erlianhot, and at an altitude of 1000 m. The deposit covers an area of 21 km², with nine porous brine-filled beds of salts (Table 3.6) containing about 11.3 million mt of sodium carbonate, and 4.5 million mt of sodium sulfate (Zhang, 1998; Li, 1997).

EGYPT

Wadi Natrun

Several sodium sulfate lakes or playas have been reported in Egypt, and one of them may have the distinction of having the longest commercial sodium sulfate production of any deposit in the world. The Wadi Natrun (also called the Wadi El Natrun or Wadi Atrun) has been known as a source of crude soda ash (trona Na₂CO₃ · NaHCO₃ · 2H₂O) since before 3500 B.C. It is a series of 2–20 playa lakes (depending on the dryness or moisture level of the period) in a northwest-trending arc fairly near the northern end of the Nile River (Fig. 3.17). Among its many individual sub-basins several contain almost pure halite, others similarly pure trona, and one contains massive and pure thenardite (Na₂SO₄). Trona has been found in the oldest Egyptian tombs, and it appears that salt and thenardite have also been recovered from the Wadi Natrun for an equally long time. There were 10 major lakes in 1970

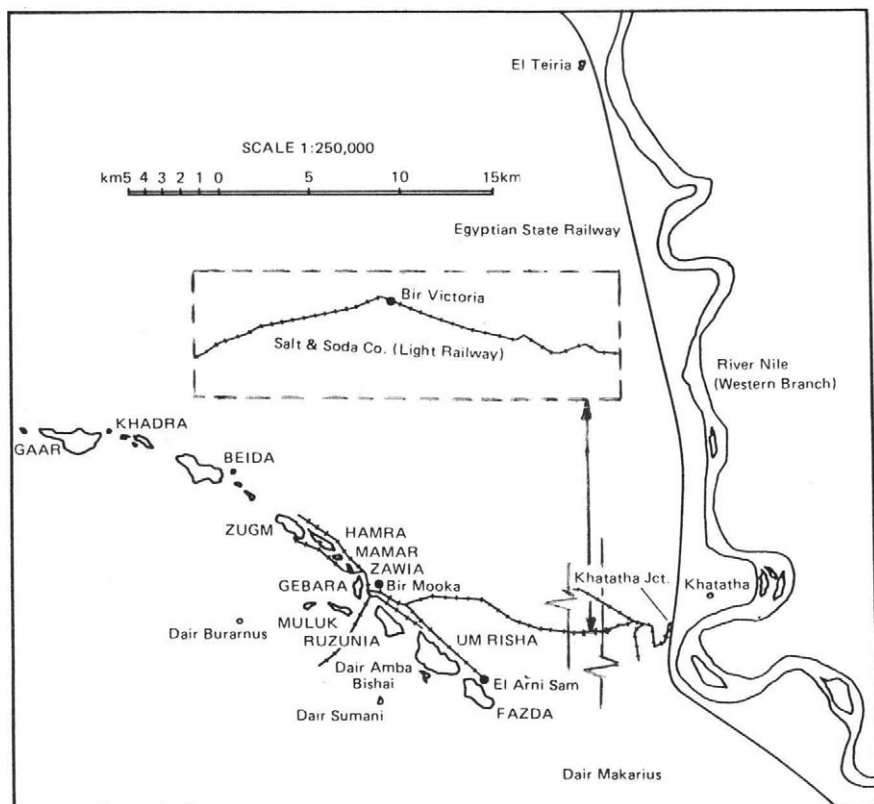


Figure 3.17 Map of the Wadi Natrun chain of lakes, Egypt. (From Garrett, 1992.)

and 12 in 1986, all with a brine high in carbonate, sulfate, and chloride, but individual lakes have quite different principal mineral deposits (Hilmy and Darwish, 1966). The lakes at each end are higher in elevation and crystallize principally trona or natron ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$). The next lower lakes in the center of the arc contain principally halite (NaCl), whereas Beida Lake is the lowest in the arc's north-center and contains massive thenardite.

The deposit is located 80 km northwest of Cairo and about 35 km west of the Nile River at an elevation of -23 m, and 32–38 m below the Nile, its probable water source. The combined area of the lakes is about 12 km^2 , they extend for 25 km within a 5-km wide band, and each has numerous springs on its Nile side with a near-fresh, high-sulfate, low-carbonate (and other salts) water. It appears that prolific sulfate-reducing bacteria have formed the ~ 2000 t/yr of trona that may have been harvested each year for the past 5500 years. The principal impurity in the trona is burkeite (0–39%; $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$), with halite (2–27%) next most common.

In the trona lakes, besides the burkeite impurity there is some thenardite and very small amounts of hanksite ($9\text{Na}_2\text{SO}_4 \cdot 2\text{Na}_2\text{CO}_3 \cdot \text{KCl}$). In 1912 trona was harvested from three lakes, four were trona preconcentrators, four had some halite harvesting, and Beida was mined for thenardite (Garrett, 1992).

Beida Lake is 1.5×0.8 km in size, with an area of 1.2 km^2 . It becomes completely dry during July and August and is covered by a 0.5-m crust of halite with some thenardite, trona, and wind-blown sand. Beneath this is a 1- to 4-m thick (average, 2 m), lenticular bed of thenardite, containing 1.1 million mt of Na_2SO_4 (Fig. 3.18) with some thin interlayers of black clay. Beneath the thenardite is more black clay. The thenardite occurs as large (3 mm–10 cm), well-developed crystals in clusters or rosettes, with a clear or slightly opaque color and a density of 2.58 g/cm^3 . More than 10 different thenardite crystal habits have been identified, all well-formed and of prismatic and pyramidal form. Various other soluble sulfate minerals have also been found in the deposit (Nakla *et al.*, 1986; Nakla and Saleh, 1985). About 45,000 t/yr of a crude product are sold from the deposit (McIlveen and Cheek, 1994).

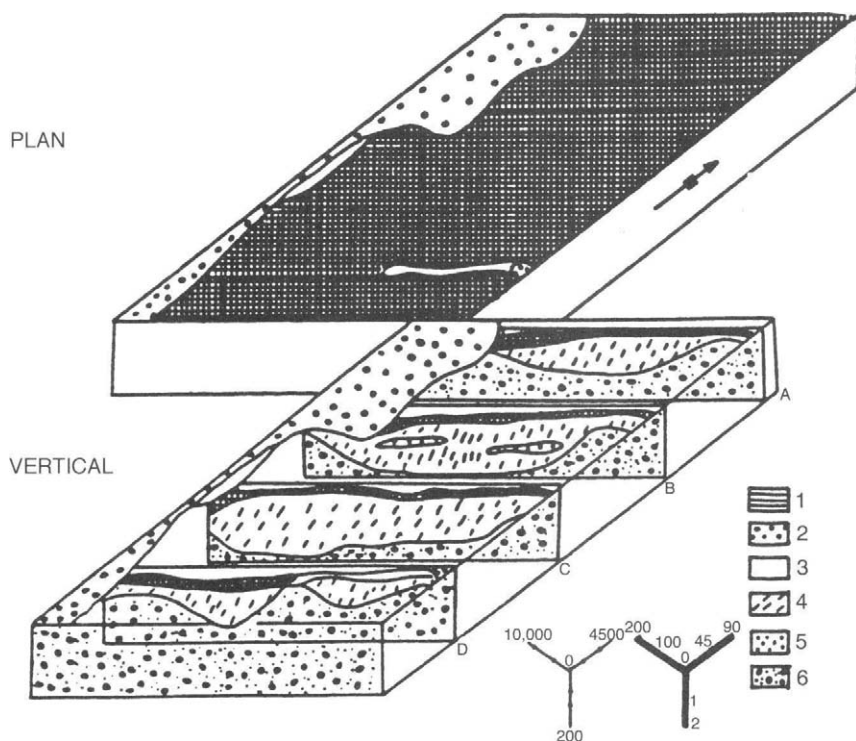


Figure 3.18 Cross section of Beida Lake, Wadi Natrun, Egypt. 1, halite; 2, brown-yellow sand; 3, halite in brown sand; 4, thenardite; 5, black sand; 6, black sandy mud. (From Nakla *et al.*, 1986, by permission of the International Mineralogical Association.)

Other Lakes

Engineering studies have been made on possible U.S. aid for the coproduction of 7500 t/yr of sodium sulfate (with 200,000 t/yr NaCl and 21,000 t/yr MgO) from *Lake Qarun* near El Faiyum, but the project has not been implemented. The brine was very dilute (8.32 g/liter SO_4), but the 226 km² lake was claimed to contain 4 million tons of Na_2SO_4 (Estefan *et al.*, 1980; Anon., 1980a). Sodium sulfate has also been reported in the *Katuree Salt Lake* north of Nyanza (Wells, 1923).

IRAN

In 1989 Iran was reported to have produced 185,000 t/yr of sodium sulfate from 13 deposits located in the provinces of Markazi, Semnan, and Teheran (McIlveen and Cheek, 1994). Prior to that, in 1977 and for the previous 20 years, up to 50,000 t/yr of a crude sodium sulfate were produced from the semiarid *Hoz-i-Soltan* valley (Fig. 3.19), near the cities of Damavand and Waramin. This basin in the Tehran–Qom area is 30 km wide, enclosed by ranges 150–200 m high containing gypsiferous marl on top of a zeolite dibase, and with four mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$)-containing subbasins in its flatter southern end between three parallel internal ridges. A perennial river, Rud-e-Shur (Salty River), flows from the northwest into the four valleys. The largest basin (Hassan) is about 3 km in diameter, has an area of 7–8 km², has sediments 60 m deep consisting of layers of mirabilite, mud, zeolites and gypsum, and is underlain by marl. The other subbasins are Gardaneh Shir, Mahmud, and Zajn, and each of the four deposits in these subbasins employed about 40 people in their operations.

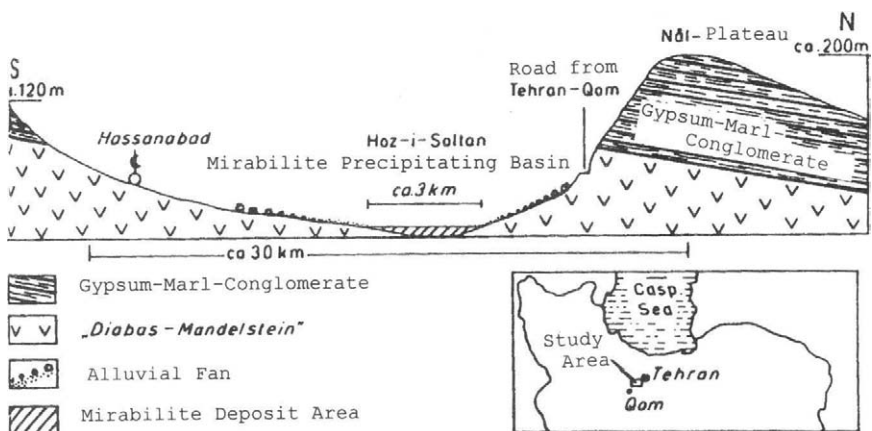


Figure 3.19 General structure and location of the Hoz-i-Soltan lakes, Iran. (From Derkmann and Mir-Mohammadi, 1977.)

Brine was evaporated in the basins each year from April 20 to the end of August (140 days), and then in the autumn and winter mirabilite was crystallized. It was harvested in the spring after the rains had washed away some of its brine and salt impurities, and then placed in 20×100 m ponds to partially dehydrate in the summer. The final product was 10–20 cm thick in the ponds and harvested with about a 10% moisture content (if dried further, there was too much dust loss and wind-blown insolubles contamination). The product was then trucked directly to local customers to be reduced to sodium sulfide (Na_2S) for tanning, or used in detergents or the glass industry (Derkmann and Mir-Mohammadi, 1977).

In the early 1970s Iran only produced about 25,000 t/yr of sodium sulfate from other sources, with some as a coproduct from *Urmiah (Reziieh) Lake's* K_2SO_4 production. The lake was 16 m deep, had an area of 6000 km^2 , contained 60 million tons of K_2O reserves, and it was being considered for up to 100,000 t/yr of K_2SO_4 and 10,000 t/yr of Na_2SO_4 production. Other lakes being evaluated for sodium sulfate operations were at Chambourak, Maharlou, and Neyriz, and brine springs at Habib Abad (Jolly, 1976). Hassani Pak (1985) noted that there were several sodium sulfate lakes in the Salt Desert, with one at its northwest edge having an area of 200 km^2 and a “0–45% Na_2SO_4 content throughout the region.” Thenardite, mirabilite, and glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$) were all present, along with halite and gypsum, in both surface crusts (mainly NaCl) and bedded deposits. Many (330) drill core samples were taken from the deposit.

MEXICO

Laguna del Rey

One of the world's larger sodium sulfate deposits, and the world's largest production of sodium sulfate in 1999, occurred at Laguna del Rey, Coahuila, Mexico. This generally dry playa is located 165 km north of Torreon (Fig. 3.20) and almost midway between Torreon, Monclova and Chihuahua in a semidesert valley of the basin and range type. In it there is a massive lenticular brine-filled crystal bed that usually begins 1–2 m beneath the surface and is 10 km long, 4 km wide, and has a maximum thickness of 35 m in its center (Fig. 3.21). Its area is 40 km^2 , its volume is 560 million m^3 , and it contains approximately 350 million mt of sodium sulfate. The primary mineral in the deposit is glauberite (averaging 50%; $\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$), with lesser amounts (20%) of astrakanite (bloedite; $\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$), 1.5% halite (NaCl), and 28.5% clay (or in chemical terms: 34% Na_2SO_4 , 7.2% MgSO_4 , 24.5% CaSO_4 , 1.5% NaCl , and 4.3% H_2O [in the astrakanite]). There is also some mirabilite (often cementing crystals of glauberite; $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) in isolated zones of the deposit. The salt mass porosity is somewhat less than 25% (15%; Guzman Paz, 1999) and is filled by a brine (Fig. 3.22) with the following average composition (wt %): 16.57 SO_4 , 4.35 Cl ,

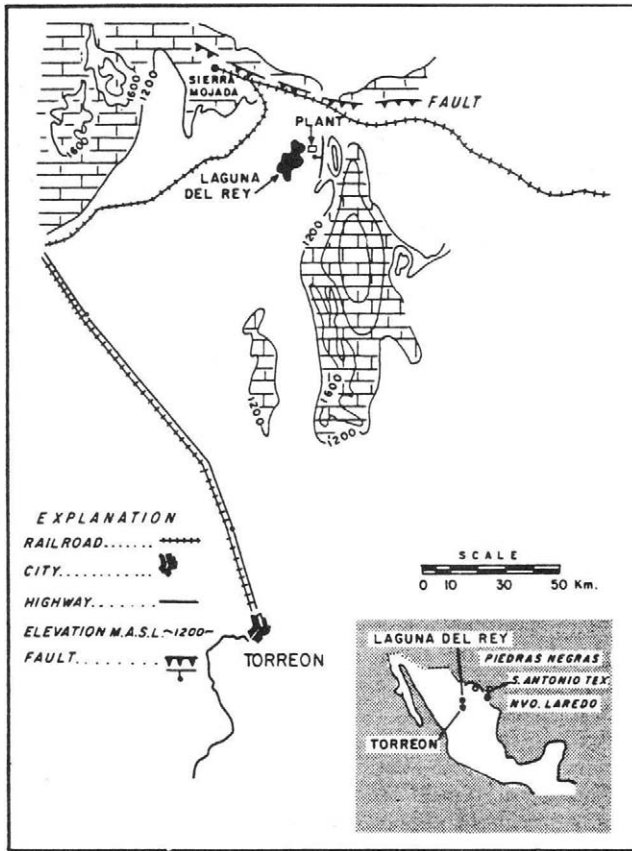


Figure 3.20 Location map of the Laguna del Rey, Mexico, deposit. (From Sanchez-Mejorada, 1986, by permission of the AIIME. First appeared in *Transactions*, Vol. 280.)

5.96 Na, 2.50 Mg, and a density of 1.30 g/cc. The deposit began to be formed about 100,000 ybp when its original lake commenced being evaporated to dryness. The area's annual rainfall is 10–20 cm/yr; it experiences a few days in the winter with temperatures of -15°C , the summer average is about 30°C , and the maximum is $>43^{\circ}\text{C}$ (Sanchez-Mejorada, 1986).

The glauberite most commonly occurs as thin, 3- to 15-mm-long, randomly oriented monoclinic flakes with a density of 2.80 g/cm^3 , and with considerable void space between the crystals. There are lesser amounts of larger crystals, being found mainly in the lower sections of the newer wells. They can be up to 2–5 cm in size and occasionally form into large clusters (Guzman Paz, 1999). The glauberite occurs in many thin beds interlayered with clay, with a thicker, purer 1- to 2-m bed near the top of the deposit. The astrakanite is usually in the form of short prismatic,

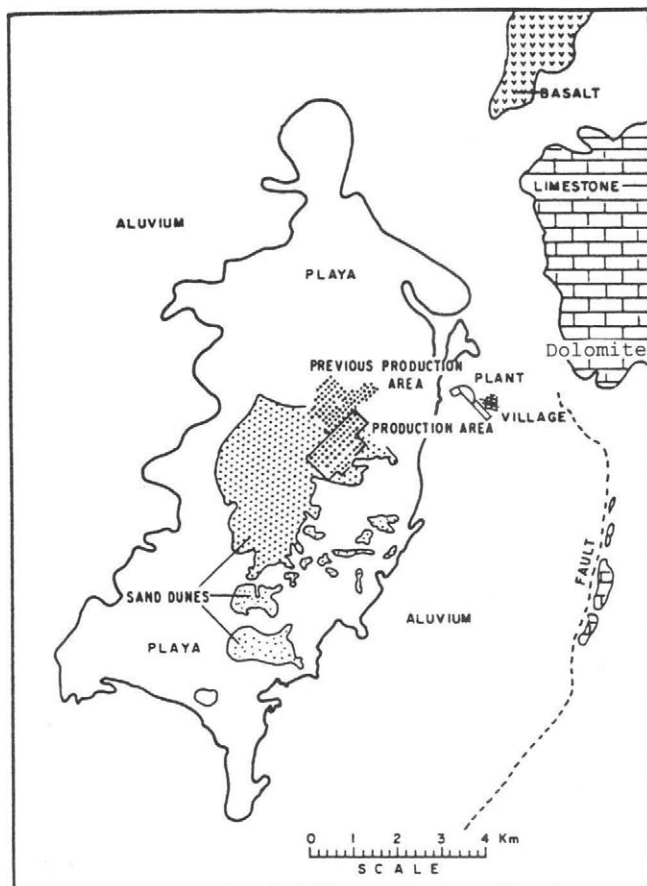


Figure 3.21 Surface features of the Laguna del Rey, Mexico, deposit. (From Sanchez-Mejorada, 1986, by permission of the AIME. First appeared in *Transactions*, Vol. 280.)

monoclinic crystals with a density of 2.25 g/cm^3 , occurring as either large clusters or amorphous masses. It is scarce in the northern end of the deposit, and more abundant to the south. There is considerable gypsum near the base of the crystal mass, and thin lenticular beds at higher elevations. A layer 1–3 m thick of red-to-green clay within the deposit almost completely divides it into two sections (Fig. 3.23). There is little astrakanite beneath the clay and large amounts immediately above it, indicating a period of vigorous inflow of surface water carrying silt and relatively high concentrations of magnesium, perhaps from acidic groundwater leaching of the dolomite hills to the east. There are also many thin lenticular, noncontinuous clay beds in the deposit (Sanchez-Mejorada, 1986).

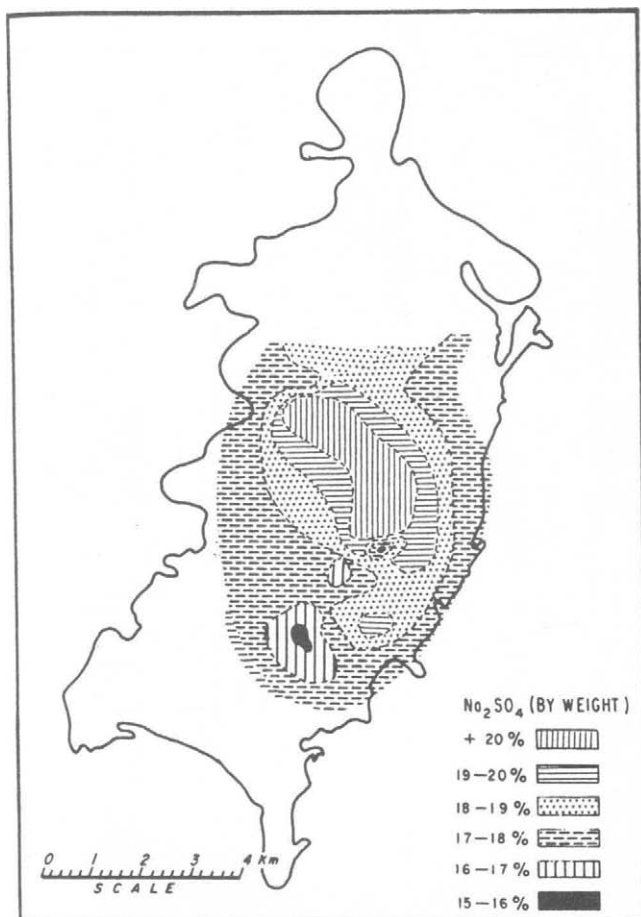
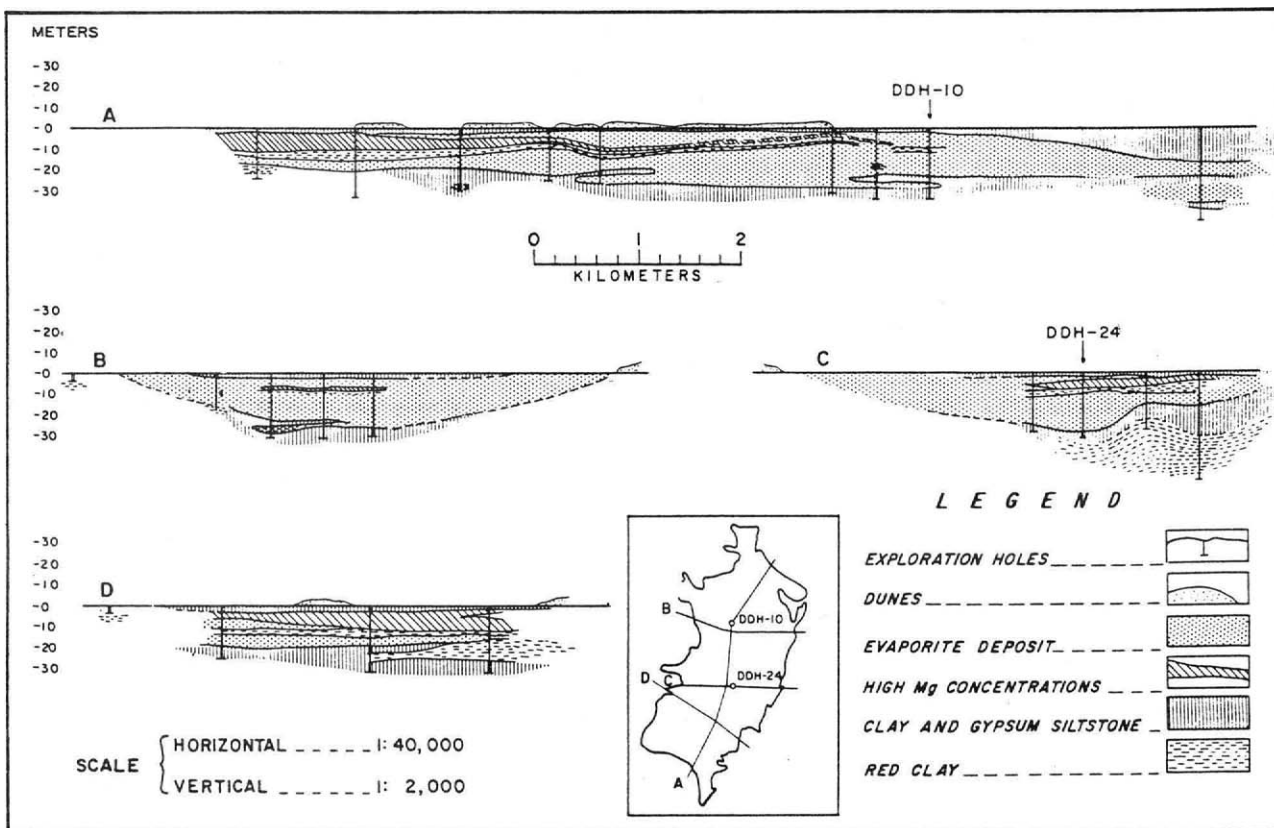


Figure 3.22 Brine concentration map of the Laguna del Rey, Mexico. (From Sanchez-Mejorada, 1986, by permission of the AIME. First appeared in *Transactions*, Vol. 280.)

The upper surface of the salts is relatively flat, except in the northern end (and a few other locations) where recent water flow has dissolved part of the deposit and caused caving. The playa's surface consists of small gypsum crystals mixed with silt, except along the edges and some places in the middle where dunes have formed. Capillary action has led to the deposition of a white salt crust on most of the lower, flatter surfaces. Beneath the crust is a layer of variable thickness that is a mixture of grayish-green silt with considerable gypsum, along with some halite and glauberite. Below that in most areas is a red clay, and then the crystal mass. The brine above the extensive clay layer in the middle of the deposit is slightly diluted



(1.2 g/cm³), whereas that below the clay is saturated (1.28–1.32 g/cm³). The entire deposit slopes slightly (about 1 m) down to the east, giving a slight artesian effect to the lower brine. The source of the deposit's sodium sulfate appears to be from the leaching of gypsum in the adjacent marine sediments, followed by ion exchange on clays of calcium for sodium. The oxidation of sulfides from the large silver–lead deposit at Sierra Mojada (to the north) must have helped, with the acid that was formed apparently also leaching some of the dolomite in the area's soil to form the high-magnesium brine (Sanchez-Mejorada, 1986).

Other Brine Deposits

There are many other saline playas in the desert regions of Mexico, and some have a high sodium sulfate content (McIlveen and Cheek, 1994; Anon., 1980b; Garrett, 1980, 1965). For instance, a sodium sulfate brine deposit has been reported near *Laguna Salada del Huso*, about 220 km northwest of Chihuahua. Its brine contains 8–14% Na₂SO₄, with reserves of 10 million t of sodium sulfate (Kostick, 1980). It had been producing 10,000–20,000 t/yr of a crude sodium sulfate product, but discontinued operations in 1999.

THE FORMER SOVIET UNION

Lakes and Playas

The area formerly contained within the Soviet Union has a very large number of playa, lake, brine, and miscellaneous sodium sulfate occurrences, and several of them are very large. The Gulf of Kara Bogaz is the largest, even though its practical reserves are somewhat uncertain. There is considerable literature on these deposits, but few of the articles are available in English, so that many abstracts have been relied on for the following discussions. Figure 3.24 shows a few locations of these deposits.

Aral Sea, Bay

There are large buried mirabilite beds in the Aral Sea (Fig. 3.25), primarily in the dry northern borders and in its upper Holocene sediments where the sea once became shallow or totally evaporated. Mirabilite (Na₂SO₄ · 10H₂O) also forms during the winter months, but most of it dissolves during the summer. In an extensive drilling program (but only to depths of <5 m) several areas of mirabilite and thenardite (Na₂SO₄; with occasional crystals of astrakanite [Na₂SO₄ · MgSO₄ · 4H₂O], glauberite [Na₂SO₄ · CaSO₄], and hydroglauberite [5Na₂SO₄ · 3CaSO₄ · 6H₂O]; Slyusareva, 1969) near the edge of the sea were discovered. In the partially isolated northern Lesser Sea two areas totaling 400 km² contained lenses >50–70 cm thick and discontinuous beds of high purity or ooze-contaminated mirabilite. It could be clear, vitreous, or dark (because of clay inclusions), and its crystal size was

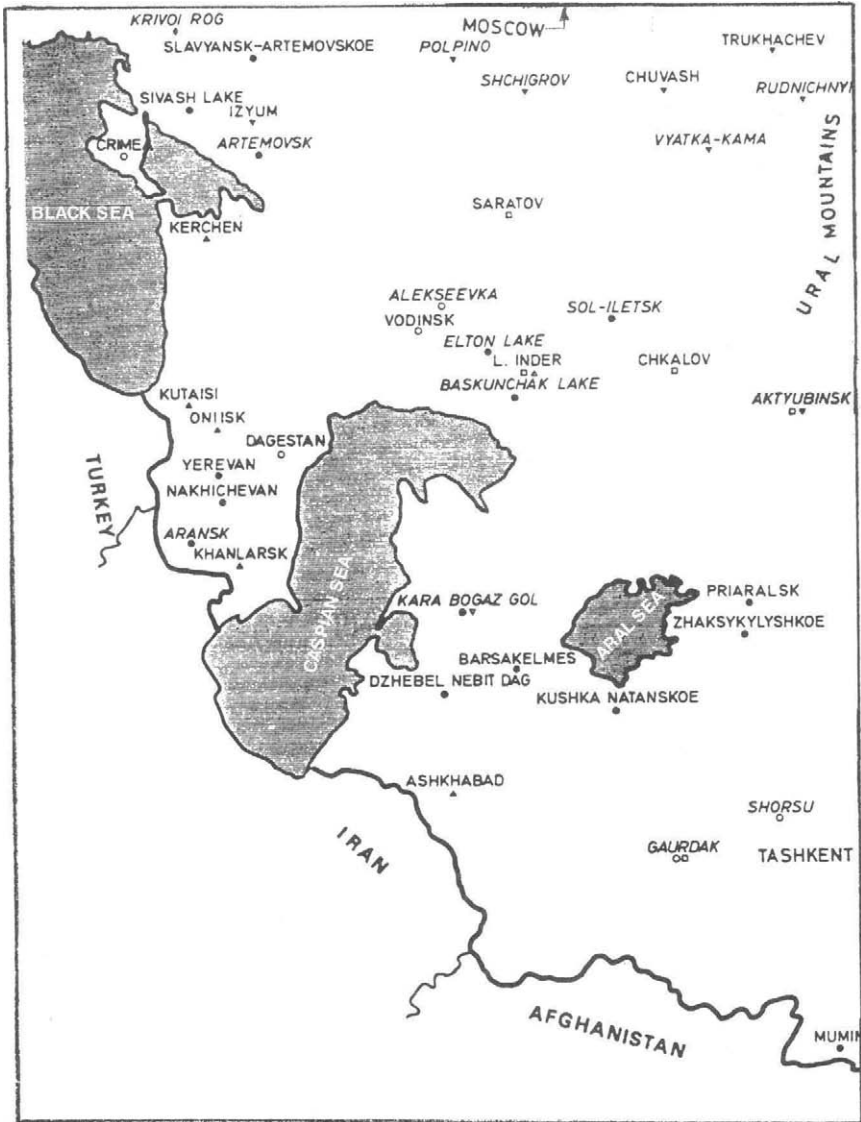


Figure 3.24 Location of some of the sodium sulfate and other industrial mineral deposits in the former Soviet Union. (▼, sodium sulfate; ●, salt; □, potash; △, borate; ■, phosphate). From Hemy (1969), reprinted with permission of *Chemical & Process Engineering*.

1–10 mm. It was covered by 1–2.5 m of gypsiferous clayey silts, and interlayered with shallow-water clastic sediments (Rubanov, 1995). In the Tushibas Bay there was a 100 km² area of 60-cm-thick mirabilite, and in the West Aral Deep one mirabilite zone was 35 cm thick with dark, coarse (up to 1 cm long) crystals. The

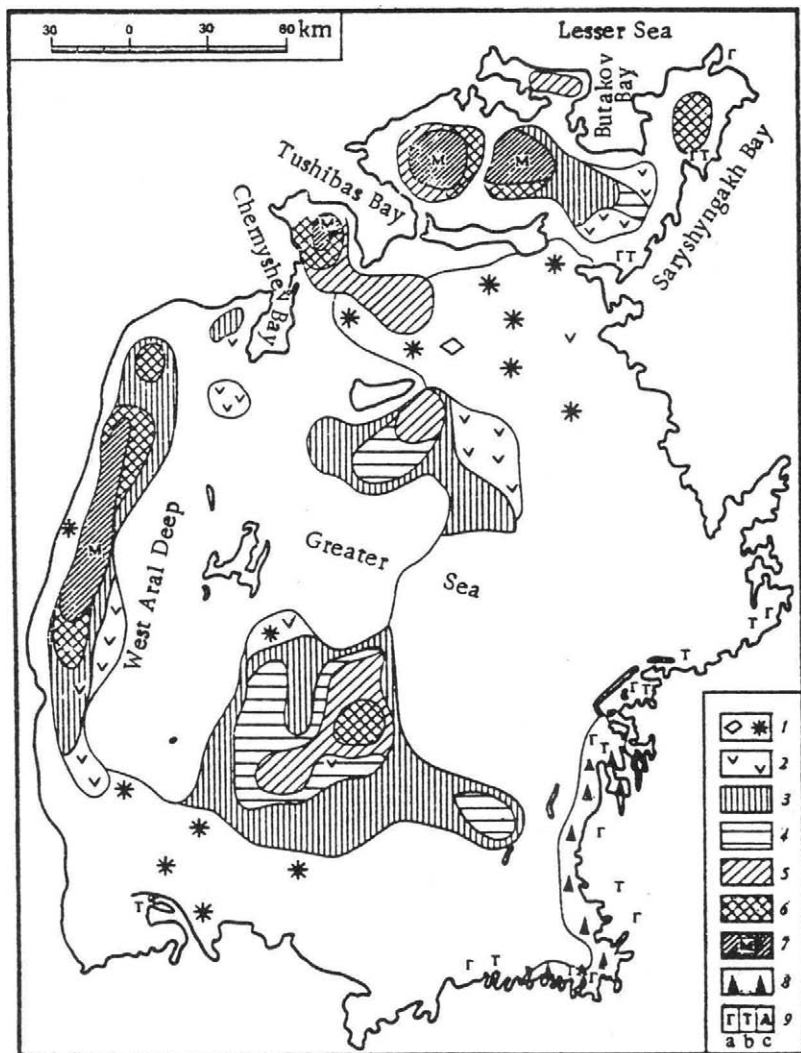


Figure 3.25 Sulfate deposits in the Aral Sea. 1, Gypsum druses and rosettes in deltaic sediments; 2–6, marine gypsum: 2, isolated crystals; 3, layer thickness: several mm; 4, up to 10 mm; 5, up to 10 cm; 6, up to 50, cm; 7, mirabilite in marine sediments; 8–9, playa: 8, gypsum; 9a, halite; 9b, astrakanite, 9c, mirabilite thenardite. (From Rubanov, 1984, by permission of the Plenum Publishing Corporation.)

total of the mirabilite areas in the Aral Sea may be about 600 km², and the equivalent sodium sulfate about 200 million t. The deposit's age is estimated to be about 1000 yr (Grokhovskii, 1978). There are also several lakes near the Aral Sea that (combined) contain an estimated 4 million mt of Na₂SO₄. The area is stated to be a "rich source" of sodium sulfate (Hemy, 1969; Ivanov, 1967; Rubanov, 1995).

Asia, Central

(Including Kazakhstan and Shor-Kan.) There are many salt lakes in central Asia that contain brines with a high percentage of sodium sulfate, and some production is claimed from several of them. More detail on various of the specific deposits is given in several other sections.

Azambur Lakes (Sakhare-Tba, Garedzhela, Kachai-Tba)

Each of these lakes contain mirabilite deposits, and the first two have commercial sodium sulfate production. They lie in parallel basins separated by low ridges, with Lake Sakhare-Tba being 2 km long and containing a perennial lake 0.5–0.7 m deep with a 0.7 km² area in its southeast corner. Its mirabilite deposit is lens-shaped and 0.1–6.6 m thick. In 1955 a 67-hole drilling program delineated the deposit and indicated a mirabilite purity of 77–95% (average 87.4%). The insolubles content varied from 1.5 to 15%, that of NaCl from 0.24 to 1.38%, and that of calcium sulfate from 1.31 to 10.80%. The clay sediments in the lake above and below the mirabilite lens also contain 5.6–20.6% mirabilite. A spring under the lake and the lake waters contain a comparatively pure sodium sulfate brine. Unfortunately, since most of its former springs have been closed, the lake is now progressively drying up. This area of East Georgia (Kakhetiya) is rich in sodium sulfate springs, and the area's sarmatian rocks are gypsum-bearing. This, plus ion exchanged sodium, perhaps provided a source for the springs (Eristavi *et al.*, 1956,1975).

Azhbulat Sulfate Lake

In this lake in the northern part of Kazakhstan as much as 40 million mt of mirabilite crystallizes each winter, starting to form when the lake waters are at 15–20°C, and reaching a maximum at about –10°C. Most of it redissolves in the summer, but the lake also has extensive mirabilite deposits. Some thenardite is observed forming in the summer, followed by the precipitation of small amounts of glauberite. It was said to be a “good sodium sulfate source” (Lyapunov, 1959; Zdanovskii, 1940a,b).

Batalpashinsk (Batalpaschinsky) Salt Lake

This lake is in the north Caucasus, located between the Black and Caspian Seas. It crystallizes mirabilite in the winter, and the mirabilite redissolves in the summer. Its area is 9 km², its volume 4.5 million m³, and it is estimated to contain 0.64–0.68 million mt of sodium sulfate. Its brine density can vary from 1.04 to 1.34 g/cm³ with an average sulfate content of 1.8–3.7% depending on the season. There is gypsum in the rocks of the lake's watershed (Laschtschenko and Morosova, 1933).

Borovie State National Park

In the Akmolinsk Region of Kazakhstan, many of the lakes and playas contain deposits of mirabilite. Sodium sulfate was produced from some of them before the area became a state park (Usova, 1944).

Borzinsk Lake

The mirabilite-halite deposit of Borzinsk Lake contain liquid inclusions that supply 0–2.66 mg of fluorine per 100 g of air-dried salts (Filippova *et al.*, 1969).

Caspian Sea: Tambukkan Lakes

(Also see Kara-Bogaz.) It has been suggested to use the nearby *Apsheron Salt Lakes* as solar ponds for producing sodium sulfate from Caspian Sea waters (Zdanovskii, 1996). There are also several sodium sulfate lakes located between the Black and Caspian Seas, such as the previously noted Batalpashinsk, and the *Tambukkan Lakes*. Each of them crystallizes mirabilite from their waters in the winter (Budrik, 1926). There are also older sodium sulfate mineral deposits at the southeastern boundaries of the Caspian Depression (Imaneev *et al.*, 1984).

Ebeity Lake

This lake, located 120 km west of Omsk, is another with a cyclic pattern of crystallizing mirabilite in the winter and having it dissolve in the summer. The brine concentration (Table 3.7) can reach 30–31% total salts by the end of summer and can begin to crystallize halite (which usually dissolves in the spring). Mirabilite deposition starts when the brine in the lake is at 18–19°C (which can be as early as August or September), and at 0°C 70% of the sodium sulfate has crystallized. At –10°C 85% has been deposited, and at –15°C 98%. At –7°C some ice crystallizes with the mirabilite, and at –21.8°C hydrohalite ($\text{NaCl} \cdot 2\text{H}_2\text{O}$) forms. The lake does

Table 3.7
Brine and Sodium Sulfate Analyses
of Lake Ebeity (wt%) (Druzhinin, 1941)

	Lake brine ^a	Sodium sulfate salts	
		Winter mirabilite	Lake deposit
Na_2SO_4	12.53	—	—
Mirabilite	—	92.89	84.17
Thenardite	—	—	11.62
NaCl	12.49	1.32	3.00
MgCl_2	2.23	—	—
MgSO_4	0.30	—	—
KBr	0.037	—	—
KCl	0.01	0	—
$\text{Ca}(\text{HCO}_3)_2$	—	Trace	—
Insolubles	—	—	1.17
Water	—	5.48	—
Sum	27.29	99.99	99.96

^aDensity, 1.2526, (25°C).

not freeze solid because of the insulating effect of surface layers of snow on top of floating mirabilite, but brine temperatures of -23.5°C have been recorded (Strakhov, 1970). The winter deposit covers the entire lake bottom 25–30 cm thick and is quite pure. Laboratory tests have shown the soluble salts in the mirabilite can be almost completely removed (i.e., to 0.08%) by a single stage of washing. The mud-covered mirabilite deposit (with some thenardite) in the lake's floor is not quite as pure, but it is extensive, and in 1941 the lake was highly recommended for commercial production (Zdanovskii, 1953; Druzhnin, 1941).

Georgia, Eastern

There are a number of sodium sulfate lakes in this area (see Azambur), with some of them containing mirabilite beds up to 6 m thick. The mirabilite is 77–94% pure, and the beds are overlain by mud. A seasonal layer of mirabilite forms on top of the mud (Strakhov, 1970; Bokii and Gorogotskaya, 1970).

Gulf of Kara Bogaz (Kara Bogaz Gol)

This large basin is a bay off of the Caspian Sea, located in about the center of its eastern side (Fig. 3.26). The gulf is connected to the Caspian Sea by a 100- to 500-m wide strait in bed rock that originally was 5 km long. Because of the gulf's very large evaporative area and only limited river inflow, an average of $21.2\text{ km}^3/\text{yr}$ of Caspian Sea brine formerly flowed through the strait into the Gulf, at rates of 25–44 m/min. The gulf is roughly ovoid in shape, extending about 200 km in a N–S direction and 150 km E–W, with an area of $18,000\text{ km}^2$, and in 1927 its average brine depth was about 8–9 m (maximum $\sim 13\text{ m}$; Strakhov, 1970). The brine level of the Caspian Sea, and consequently this gulf, however, has varied considerably over the years, and periodically salts have been deposited in the Gulf as its brine evaporated to a high concentration. It is estimated that about 0.5 million years ago the first salts were crystallized, and since that time three separate layers have formed, with the last one still being deposited. The upper layer is at depth of 0–0.3 m and up to 3 m thick; the middle layer is at a depth of 5–8 m; and the lower layer is at a depth of 14–18 m. Both the second and third layers are 3–18 m thick. Gypsiferous–carbonatic muds separate the salt layers by 2–5 m (Kurilenko *et al.*, 1988; in a second article (1987) they quoted first salt layer, 0–4 m thick; then 3–8 m of mud; second salt layer, 2–10 m thick; then 4–7 m mud; and finally the third salt layer is up to 6 m thick).

Salts Deposition

The salts were laid down in a generally sequential, radial pattern from the quite narrow inlet from the Caspian Sea, and became somewhat thicker in the northeast corner, indicating that it was a low area. There was also a disrupted central band where groundwater appeared to preferentially enter the gulf. The deposition sequence started with much of the relatively small amount of carbonate in the brine being deposited, first as calcite, and then as hydromagnesite ($\text{MgCO}_3 \cdot 2\text{H}_2\text{O}$). Gypsum crystallized next, and since over time all of the Gulf had been flooded with only mildly evaporated brine (gypsum forms on average after a 6% evaporation of Caspian Sea

Table 3.8
Gulf of Kara Bogaz Brine Analysis (wt%)

	Second bed average, brine, 1927 ^a	End liquor, surface			Second, third, salt layers ^{b,s}	
		982 ^a	Center ^b	Edge ^{b,f}	Edge ^f	Center
NaCl	9.52	2.0–2.50	0.6 ^d	4 ^c	3.2 ^c	4 ^c
NaSO ₄	4.83	2 ^c	1 ^c	3 ^c	4.8 ^c	1.2 ^c
MgSO ₄	5.28	6 ^c	2.5 ^d	5 ^c	4 ^c	6 ^c
			3 ^c			
MgCl ₂	—	20–24	27.2	10 ^c	8 ^c	20.8
			27.8 ^d			
KCl	0.21	— ^e	— ^e	— ^e	— ^e	— ^e
Br	0.12–0.18	0.76–1.17	—	—	—	—
TDS	20.0	33–34	32;31.4 ^d	22	20	32
Density (g/cm ³)	1.20	—	1.297 ^d	—	1.23–1.30	—
Viscosity	—	—	9.6 ^d	—	—	—
(centipoise)						

^aFedin (1987).

^bKurilenko *et al.* (1988a).

^cAuthor's estimates.

^dStrakhov (1970). Also 0.5% Ca(HCO₃)₂.

^eKCl included with the NaCl.

^fDiluted by groundwater.

^sAfter considerable end liquor drawdown.

(along with the always dominant halite). Glauberite was also formed by the reaction of strong high-sulfate brines with gypsum. Much later as some of the glauberite was leached, and these waters were cooled, limited amounts of mirabilite were also crystallized from the glauberite. Most of the mirabilite, however, crystallized in the winter, and some of it floated and was blown by the wind toward the shores. Some also became buried, resulting in the formation of a peripheral, near-shore, comparatively high-sodium-sulfate zone. In the north it is estimated to be 5–10 km wide (Kurilenko *et al.*, 1982), with each of the buried beds containing 1–5 layers with a high-glauberite content alternating with 1–3 halite layers and 1 or 2 halite-astrakanite layers, each 0.5 to 2–4 m thick. The high-halite beds have a porosity of 30–35%, the high-glauberite beds 20–25%, and each horizon is filled with brine (Table 3.8; Grokhovskii, 1978; Kosolov *et al.*, 1969, 1974).

The thick portion of the second salt bed in the Gulf's northwest corner has been classified into four areas, as indicated in Table 3.9 and Fig. 3.27. The first zone, along the rocky shores of the gulf, contains mainly halite and glauberite crystals, and a relatively rich sodium sulfate brine. It has been formed by the inflow of high-Ca aquifers into the sulfate salts to convert them into glauberite, followed by some leaching. The second zone extends further into the gulf, tapering to extinction at each end. It has also been contacted by strong brine and groundwater, converting

Table 3.9
Idealized Composition of Some of the Second Salt Layer's High-Sulfate
Beds in the Gulf of Kara Bogaz^a

Zone ^b	Average thickness (m)	Mineral content (%)			Brine composition (%)				
		Halite	Glauberite	Astrakanite	SO ₄	Cl	Na	Mg	K
1-1	3.9 m	40.2	53.9	3.9	5.4	22.9	19.8	8.5	0.25
1-2	7.3	39.3	56.1	4.6	7.6	21.5	16.9	12.2	0.40
2-1	8.0	30.7	44.1	24.9	7.7	21.9	13.6	16.0	0.53
2-2	5.4	3.6	60.1	36.3	—	—	—	—	—
3	4.2	4.3	92.6	3.1	8.3	21.2	12.1	17.4	0.57
4	5.1	5.5	62.0	33.5	8.3	21.2	11.2	18.3	0.56
Ave.	5.6	20.6	61.5	17.7	7.5	21.7	14.7	14.5	0.46

^aKurilenko *et al.* (1988).

^bSee Fig. 3.27.

epsomite to astrakanite, but less of the sulfate salts to glauberite. The third zone appears to represent a low point in that area of the gulf, with semiporous sediments underneath to allow more than average brine seepage. High-Ca surface water appears to have converted all of the sulfates to glauberite in this zone, and leached

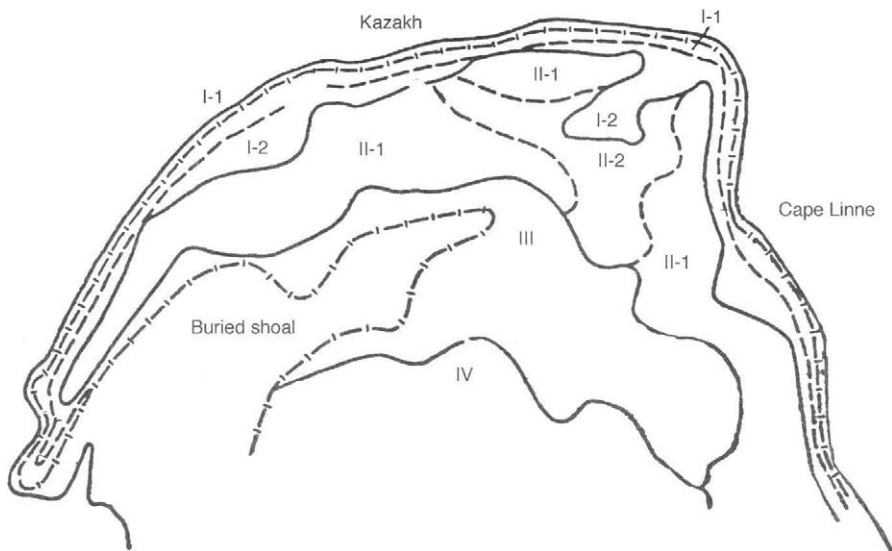


Figure 3.27 Mineralized zones in the second bed of the Gulf of Kara Bogaz. I, halite–glauberite; II, halite–glauberite–astrakanite; III, glauberite; IV, glauberite–astrakanite. (From Kurilenko *et al.*, 1988, reprinted with permission of *International Geology Review*, Vol. 30, No. 11, pp. 1238–1245. ©V.H. Winston & Sons, Inc., 360 South Ocean Boulevard, Palm Beach, FL 33480. All rights reserved.)

most of the halite. The brine in the void space has the composition of the Gulf's end liquor and has a high density. A small zone next to it has also had heavy halite leaching, but somewhat less astrakanite conversion (Kurilenko *et al.*, 1988).

Changes in the Gulf

Before the present dry period, considerable glauber salt accumulated each winter along the gulf shores, crystallizing when the brine temperature was $<6^{\circ}\text{C}$. "Vast quantities" were reported, "containing no iron and only 0.03% MgSO_4 and CaSO_4 ." Most of it dissolved in the summer, but during some periods in restricted periphery areas (especially in the southwest) there was a net accumulation of about 1 cm/yr. Some of this mirabilite was later converted to glauberite. The presence of these deposits led to a floating drilling program being conducted in 1934, and the deposits noted above were discovered. That same year, however, a more arid cycle commenced in the region, and the Caspian Sea's level began to drop. By 1952 the Gulf's surface brine area was only 8000 km^2 , and a more detailed drilling program was conducted over a 100 km^2 dry area in the northwest. From it a 26.5 km^2 zone was designated for commercial production near the Kurguzul inlet, and a second area was indicated in the Sartassk Cove. As the arid period continued the Caspian Sea's normal brine concentration of 0.8–1.3% soluble salts began to increase (up to ~ 23 g/liter), endangering its sturgeon and other fish populations. Because of this in 1980 the rivers that fed into the gulf were diverted directly into the Caspian Sea, and an earthen dam was constructed across the straits between the gulf and sea. This isolated the gulf, and by 1983 it was essentially dry. The salts that had been present in the brine were deposited on the surface in the usual halite–epsomite–astrakanite sequence. Additional drilling was then conducted over a 10,000 km^2 area.

Commercial Operation

The glauberite, astrakanite, and mirabilite found in the drilling surveys were claimed to total perhaps 2 billion t of equivalent sodium sulfate. Because of the great area covered this would appear to be somewhat speculative, but even if true, the minerals' very scattered and extended locations in thin beds or disseminated crystals would greatly limit the possibility of their recovery. However, the two restricted areas in the northwest corner of the gulf with thicker and more consolidated mineral zones (with perhaps 10 million t reserves) have allowed the large-scale production of sodium sulfate since 1952, and the plant was expanded and modernized in 1973. Brine was pumped from the second salt layer at a depth of 4–15 m, with an initial composition as shown in Table 3.8. This brine had been formed largely by the dissolution of glauberite and mirabilite (and was not Caspian Sea end liquor), and thus was much easier to process for sodium sulfate (a simple salting-out process with NaCl was used). The sodium sulfate capacity of the plant in 1973 was 100,000 mt/yr, increased by 35,000 mt/yr in 1988 (Levine, 1988), and in 1987 it produced about 35% of the country's natural sodium sulfate output, as well as all of the country's magnesium chloride and magnesium sulfate (Fedin, 1987, 1982).

Over the years that the gulf's surface brine level was shrinking, the plant suffered a continually reduced brine quality. This occurred because of a rather surprising

design decision, pumping the plant's brine supply from a single well (four others were available as stand-bys) at a rate of $6\text{--}12 \times 10^6 \text{ m}^3/\text{yr}$ (2700–5500 gal/min). This very high pumping rate caused a rapid drawdown near the well, gradually extending outward until an area 15 km in diameter had suffered severe surface leaching and cavity formation. It caused much of the brine to come from the surface, which could either be dilute (causing the surface leaching) or very high in magnesium chloride and low in sodium sulfate (the end liquor from the gulf brine's evaporation). Both factors produced a plant brine that became progressively more expensive to process, and because of short-circuiting and bypassing of large areas (in favor of easier flow paths at this high rate), it essentially lost the majority of the reserves in the affected area. Had the pumping rate been 20–40 times less per well, there would have been very little drawdown, and the well field could have produced the near-original brine until most of the deposit was recovered in that area. The cost of this expanded well field would have been only nominally greater than that of the single well.

In a futile attempt to help the plant and minimize a severe dust problem from the gulf's dry surface, a large amount of brine from the Caspian Sea has been pumped into the gulf since 1984. However, it has not helped the plant, and it may have actually hurt the operation since it covered only part of the gulf's area and supplied more readily available high-MgCl₂ and liquor to be drawn into the well. There should always be enough brine in the subsurface salts from normal water inflow to allow the plant to receive its brine supply without any further pumping from the Caspian Sea. However, if the gulf were desired to become a salt reservoir for the sea, a deep-water inlet pipe in the sea could drain a more concentrated brine to the gulf for evaporation and salt deposition, without harming the sodium sulfate operation. The dust problem would appear to be unsolvable, but in time should subside as rains leach the surface sodium sulfate efflorescence and leave the more stable halite.

Many studies have also been made on the possibility of using Caspian Sea brine or evaporated liquor for sodium sulfate production (i.e., Sedelnikov *et al.*, 1979). One such method was practiced unsuccessfully ("because of variable brine concentrations") starting in 1929, as was small-scale harvesting of the winter's surface mirabilite. A very large number of articles have also been written on studies concerning the gulf's mineralization, its brine and salts' trace element content, and many other aspects of the deposit (e.g., Andriyasova *et al.*, 1971a,b–1975; Azarova *et al.*, 1975; Bailieva *et al.*, 1969–1974; Blyumberg and Nikolaev, 1947; Buinevich *et al.*, 1987; Chilingar, 1956; Dzents-Litovskiy, 1956, 1966; Fedin, 1992–1972; Gavilova, 1984; Kitaigorodskii, 1925; Korotkevich and Kurilenko, 1983; Lepeshkov *et al.*, 1969; Mekhtieva, 1980; Nuryagdyev and Sedelnikov, 1966; Podkopaev, 1923–1930; Pustynnikov *et al.*, 1975; Shavarts, 1987; Shreders, 1938; Spivak *et al.*, 1984; Vakhrameeva, 1968; Zabrodin, 1974).

Ilmen Wildlife Preserve

This area contains dry lakes with a number of saline minerals, including thenardite and astrakanite (Chesnokov, 1981).

Kuchuk Lake

A sodium sulfate production “combine” has been established at this mirabilite-brine deposit on the Kulunda Steppe, southwest of Novosibirsk, western Siberia, in the Volga region (Altai Territory). The lake’s area is 160 km², and in 1938 it was estimated to contain about 540 million mt of equivalent sodium sulfate. A thick glassy mirabilite deposit (“an enormous lens”) occurs in the lake as two layers, the upper one being 3 m thick, and both containing <1% other soluble salts. The mirabilite is overlain by a 0.05- to 2-m layer of mud and salts containing 40.5% salts, 20.6% water, and 38.9% insolubles (including considerable gypsum). Much of the mirabilite in this layer has been transformed into thenardite, and the deposit also contains some halite, glauberite (Na₂SO₄·CaSO₄), hydrohalite (NaCl·2H₂O), and epsomite (MgSO₄·7H₂O).

Mirabilite crystallizes from the lake brine during the winter and cool summer evenings (estimate to be 340–580 thousand mt/yr), and then during the warm summer months some of it converts to thenardite. A limited amount of insolubles accumulates with the crystals, forming thin layers of mud with the thenardite. Brine from the lake has a 10–31% soluble salt content, depending upon the season and lake level (Table 3.10), and every 3 years at the end of summer it is pumped to solar ponds to crystallize mirabilite during the autumn. The residual brine in the ponds is returned to the lake before winter sets in, and the ponds are harvested as needed for the production of sodium sulfate (Charykova *et al.*, 1996). For most of the year the brine is of the magnesium chloride type, but during the summer it changes to a sodium sulfate base because of the dissolving of the underlying mirabilite, thenardite, and glauberite. During the period 1965–1985 the lake level seriously declined (Stankevich *et al.*, 1984–1990; Tyuleneva *et al.*, 1986; Batalin and Ediger, 1971; Nikolskaya *et al.*, 1964; Lyapunov, 1962; Bukshtein, 1949).

Kulunda Steppe Region (Lake Kulunda)

There are at least three major sodium sulfate lakes in the Altai Republic in addition to Lake Kuchuk (see above), containing buried mirabilite deposits covered by a layer of clay. Above the clay there is a bed of halite, and above that there may

Table 3.10
Brine Analysis for Lake Kuchuk (wt%)^a

	Na ₂ SO ₄	KCl+NaCl	MgCl ₂	MgSO ₄	Mg(HCO ₃) ₂	Density	Viscosity
Spring	6.64	15.55	4.39	—	—	1.218	2.33
Early winter	0.27	18.23	4.66	—	—	1.178	1.85
Midwinter	—	1.20	25.70	2.50	0.50	1.310	8.30
Late winter	—	—	32.80	1.70	0.40	1.332	11.90

^aStrakhov, 1970.

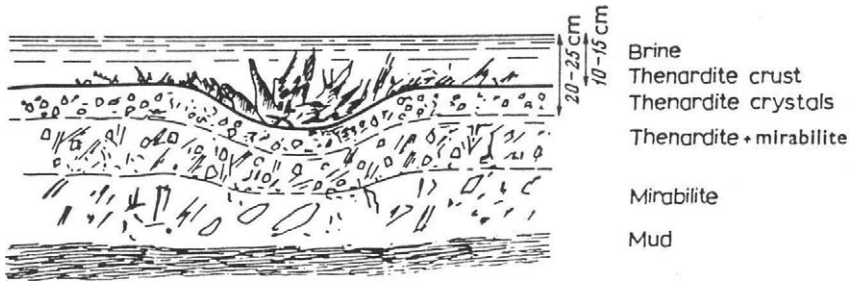


Figure 3.28 Typical sodium sulfate depositional structure in Bolshoe Mormyshanskoe Lake. (From Strakhov, 1970, by permission of Plenum Publishing Corp.)

be thenardite lenses. The playa surfaces contains many 0.5–25 m (typical 0.5–2 m) diameter dishlike basins (i.e., the typical “spotted lake”), and in these depressions the salts are primarily thenardite (Gorbov, 1950). It has been observed at the *Bolshoe Mormyshanskoe Lake* (Fig. 3.28) that in the evenings early in August coarse mirabilite crystallizes and falls to the bottom. During the days the brine temperature rises because of both convection and direct radiation absorption by the muddy crystals on the bottom, changing some of the mirabilite to thenardite (in contact with the NaCl-saturated lake brine), particularly in the small, shallow (<10–25 cm) depressions (Strakhov, 1970; Sosipatrov, 1958). This region is stated to be a “major source” of sodium sulfate, including the *Altay Kray* area, where a number of lakes have waters rich in sodium sulfate (Sokolov *et al.*, 1981).

Maloe Yarovoe Lake

This lake is in a closed basin with an arid climate and a precipitation rate of 500–600 mm/yr. Its brine is of the sodium sulfate type, but also contains NaCl and MgSO₄. Mirabilite crystallizes in the winter in amounts of up to 1 million t/yr, and much of it redissolves in the summer. The mirabilite deposit in the lake floor is not of sufficient purity to be commercially processed, but about 3 million mt of sodium sulfate are estimated to be present in the lake’s brine (Batalin, 1974).

Marfovka Lake, Crimea

This lake on the Kerch Peninsula in the Crimea deposits a 2- to 3-mm layer of mirabilite in its bottom during the winter, which converts to thenardite in the summer. There are also some permanent mirabilite druses on the bottom that are 7–8 cm long, and up to 1.5 cm wide. Typical brine and salt compositions in the lake are shown in Table 3.11 (Ponizovskii *et al.*, 1958). Thenardite efflorescences coat the rocks on the southern slope of the adjacent Crimea Mountains around sulfate-bicarbonate springs (Suprichov and Albov, 1966).

Table 3.11
Brine and Salt Analyses from Lake Marfovka (wt%)^a

	Na ₂ SO ₄	NaCl	MgSO ₄	CaSO ₄	Ca(HCO ₃) ₂	H ₂ O	Total
Brine, 1933	0.63	4.74	1.92	0.22	0.024	—	7.53
Brine, 1948	1.50	10.64	3.84	0.19	0.22	—	16.39
Thenardite	94.18	2.29	2.41	0.65	—	0.47	100.00
Mirabilite	37.27	3.66	2.22	0.36	0.53 ^b	55.96	100.00

^aPonizovskii *et al.*, 1958.

^bInsolubles.

Shor-Kan (Central Asia)

The Shor-Kan mirabilite deposit occurs as a salt marsh in the Kamysh-Kurgan salt region of Tajikistan and contains a saturated sodium sulfate brine in its void spaces. Its surface area is 0.3 km², and it is covered with a crust of salts. The central portion of the mirabilite deposit is 200 × 175 m in area, and the mirabilite is up to 5.5 m thick. Its narrowest zone is 200 × 20 m; the salts are 3–4 m thick and contain 44–55% Na₂SO₄ and 2–12% NaCl. In the central section the mirabilite analyzes as 64–83% Na₂SO₄, 2–5% NaCl, 9–19% insolubles, and contains some thenardite, glauberite, and gypsum (see Table 3.12). There are mineral springs in the marsh, and both they and the interstitial brine contain a relatively pure sodium sulfate brine. Some thenardite occurs as intercalations in the gypsiferous rocks (clay–sandstone–gypsum) of the adjacent Makhautau Range (Vorobev and Kadysev, 1951; Feodotiev, 1945).

Table 3.12
Analyses from the Shor-Kan Sodium Sulfate Deposit^a

	Deposit (wt%)		Adjacent brine (g/liter)	
	Average	Range	Average	Range
Na ₂ SO ₄	51.84	21–83	121.76	110–144
NaCl	7.56	2.2–11.0	159.87	134–189
Ca	3.39	1.1–5.2	—	—
Mg	0.22	0.04–0.37	—	—
HCO ₃	0.70	0.31–0.91	—	—
H ₂ O	15.53	1.2–47.6	—	—
Insolubles	20.76	2.4–42.2	—	—
MgSO ₄	—	—	9.99	8.6–11.7
CaSO ₄	—	—	7.60	4.8–9.7
Ca(HCO ₃) ₂	—	—	0.36	0.31–0.47
Total	100.00	—	299.49	287–320

^aFeodotiev (1945). The salts were briefly dried at a low temperature.

Siberia, Eastern and West-Central

There are a large number of sulfate and carbonate lakes in the southern part of eastern Siberia, often with a high sodium chloride content. Most of them contain deposits of mirabilite, and often there is also some thenardite (Vlasov, 1969). There are similar lakes in the Krasnoyarsk region of west-central Siberia.

Tajikistan Loess

In the younger loess of this area mirabilite and thenardite are the predominant water soluble salts contained in the formation (Pilosov, 1968).

Tengiz Lake

This lake in central Kazakhstan is another with a cyclic pattern of mirabilite crystallization and redissolving. With it the winter mirabilite crystallization starts when the brine temperature reaches 10°C (Strakhov, 1970).

Transbaikali: Selenga Lake

The southeastern region of Transbaikali contains 79 saline lakes, 66 of which are of the carbonate-sulfate type and deposit considerable mirabilite. Thirteen lakes are only of the sulfate type, with four nearly saturated, and the remainder being brackish. In the winter they all crystallize both mirabilite and hydrohalite ($\text{NaCl} \cdot 2\text{H}_2\text{O}$). In only one of the lakes do salts deposit in the summer, crystallizing halite and thenardite (Vlasov and Filippova, 1973). The *Selenga Sulfate Lake* in eastern Transbaikali is typical of these lakes. In the fall when the brine cools to 14–16°C, mirabilite begins to crystallize, and when the brine cools to –4°C the first ice crystals appear, eventually to form a solid crust. In the spring the ice melts and the mirabilite begins to dissolve. By summer it is totally back in solution, evaporation removes the year's accumulation of water, and the cycle is repeated (Vlasov and Gorodkova, 1961).

Transkuban Plain Loess

Among the lacustrine minerals in these loess, thenardite is third in abundance after calcite and halite. Some mirabilite is also present (Murzabekov, 1975).

Other Lakes

Typical structures of the sodium sulfate lakes in the former Soviet Union are shown in Fig. 3.29. A few of the literally hundreds of other lakes with sizable mirabilite, thenardite, glauberite, or astrakanite deposits are listed below: *Baichunas, Balkhash Region* (thenardite; Beremzhanov, 1967); *Dzhamansor, Ili River Valley* (Stankevich *et al.*, 1984); *Ishimbayevo, Issyk-Kul Lake* (Vertunov, 1969); *Karabotan, Kara-Kul* (Kadyrov *et al.*, 1966); *Karaganda district* (Lezir, 1967); *Kara-Tau foothills* (Grokhovskii, 1970); *Kok-Tyube, Korduvanskoe Lakes* (Lyapunov, 1959); *Kurgan-Tuz, Maloe Korduvanskoe, Mullaly-Tuz, Southern Kazakhstan, Torei Lakes* (Shmideberg,

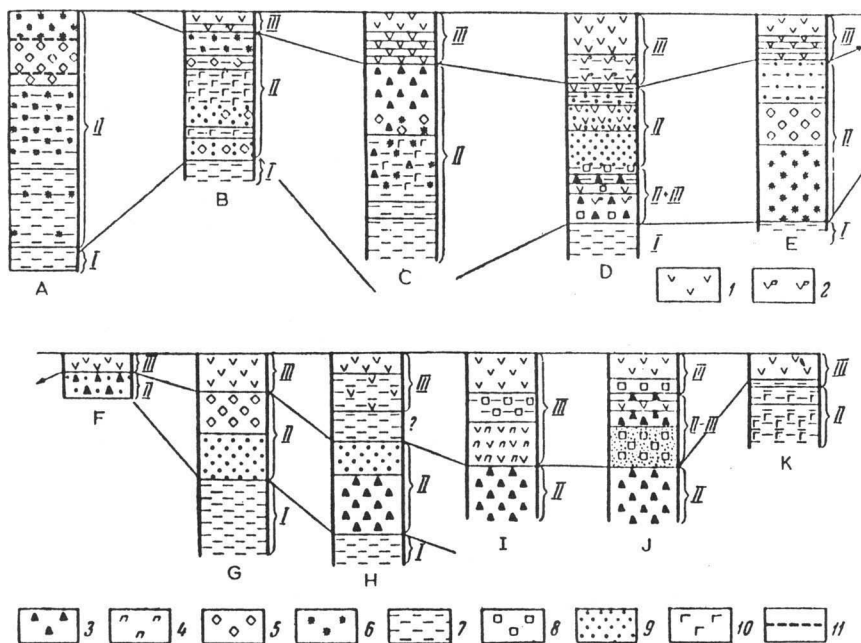


Figure 3.29 Stratigraphy of several sodium sulfate lakes in the former Soviet Union. A, Mormyshanskoe; B, Dzhamansor; C, Tuz-Kul; D, Mullaly-Tuz; E, Kok-Tyube; F, Aral; G, Karabotan; H, Baichunas; I, Maloe Korduvanskoe; J, Bolshoe Korduvanskoe; K, Kugan-Tuz. Depositional stages: I, carbonate; II, sulfate; III, chloride. Symbols 1, recent halite; 2, permanent halite; 3, astrakanite; 4, epsomite; 5, thenardite; 6, mirabilite; 7, mud; 8, uncementated halite; 9, glauberite; 10, gypsum; 11, thenardite crust. (From Strakhov, 1970, by permission of Plenum Publishing Corp.)

1966); *Tuz-Kul* and *Tuz-Kyr Lake* (Godlevsky, 1939; the nonreferenced deposits were noted by Strakhov, 1970).

High-Sodium-Sulfate Waters

Baikal Rift Zone

Hot springs in the Baikal Rift zone contain waters of the sulfate–bicarbonate type and form deposits in their mantles containing thenardite and glauberite. Both minerals have an anomalously high fluorine concentrations (up to 2.66% F; Fleshler and Yurgenson, 1973).

Bashkir

High-sodium-sulfate waters with adjacent glauberite deposits have been found in western Bashkir (Popov, 1975).

Chul-Adyr

A mirabilite deposit has been formed from the springwaters at Chul-Adyr in the Almaty region of Kazakhstan. The brine contains 23.90% NaCl, 2.40% SO₄, and 0.05% Mg, and the deposit 61.80% SO₄ (Dzhusipbekov, 1997; Nikolskaya *et al.*, 1997).

Crimean Mountains

High-sulfate and sulfate–bicarbonate waters are found in different parts of the southern slope of the Crimean Mountains. They have left sodium sulfate efflorescences on the rocks of the Taurian formation (Suprichov and Albov, 1966).

Dnieper–Donets Artesian Basin

The groundwater is soft in this basin to a depth of up to 1100 m. It is of the sulfate type, and at greater depth changes to a bicarbonate base. Saline water occurs below it with a relatively sharp boundary between the two zones (Romanyuk *et al.*, 1973).

Kungurian Sodium Sulfate Waters

The Permian Kungurian formation at Levshino on the western slope of the Ural Mountains contains sodium sulfate waters (Table 3.13). It is speculated that the sulfate content of the water has been obtained by leaching gypsum in the area's rocks, followed by calcium ion exchange with high-sodium marine rocks (marl and clayey dolomite) that the waters later contacted (Kuznetsov, 1941).

Moscow Artesian Basin

Sodium sulfate occurs in the oil and gas waters in the northern part of the Rassolnaya and Kosmach areas of the Ukraine. The total salt content is 3–50 g/liter (Nikolayev, 1975).

Table 3.13
Analysis of the Waters of the Kungurian Deposit at Levshino^a (g/liter)

	Water at various depths	Samples over a 2-yr period ^b	High-sulfate well	
Na	2.592	—	Na ₂ SO ₄	7.70
Ca	0.435	0.466	NaCl	5.77
Mg	0.299	0.279	KCl	2.46
SO ₄	5.090	5.058	MgSO ₄	1.97
Cl	1.790	1.685	CaSO ₄	1.17
HCO ₃	0.157	0.161	CaCO ₃	0.16
TDS	10.829	10.895	TDS	19.23
Depth(m)	10.8–56.0	22.3–56.0	Depth(m)	32–40

^aKuznetsov (1941). The water in a clayey-dolomite strata (only) contained 18–20 mg/liter of H₂S. All waters also contained 3–5 ppm Br and 0.1–1 ppm I.

^bWith extensive pumping.

Ural-Volga Region

The accumulation of sodium sulfate in the groundwaters of this region has been attributed to the leaching of gypsum by NaCl-containing water, followed by cation exchange of the calcium on other rocks to liberate additional sodium (Popov, 1990).

Volga-Kamskiy (Kama) Artesian Basin

Sodium sulfate dominates in the artesian waters of this basin (Popov, 1985).

Volyn-Podolian Border of the Russian Platform

Sodium sulfate waters occur in the aquifers of this area (Kozak, 1968).

Miscellaneous

Various articles have been written on the general subject of high-sodium sulfate waters, such as by Chernikov *et al.* (1994).

SPAIN

Madrid Basin

Several areas of Spain contain a number of sodium sulfate lakes, playas, or springs that have apparently received their high sodium sulfate content from the leaching of the country's thenardite-glauberite deposits (Ordonez *et al.*, 1982). None of them (or others), however, appear to be of a sufficient size to be potential sodium sulfate deposits. In the Tajo River valley (in the Madrid Basin of central Spain) there are lakes at *Carcaballana* (Villamanrique de Tajo), *Espartinas* (Ciempozuelos), and *Tirez* where some production has been obtained by the winter cooling of brines. Other lakes in the area include *Altillo* (1 km² area), *Lillo*, *Pajaros*, *Quero*, *Salicor*, and *Villacanas*. *Tirez* has an area of 0.8 km² and contains primarily mirabilite (Na₂SO₄ · 10H₂O), but also significant amounts of thenardite (Na₂SO₄; some crystals are greater than 1 cm in size), and some astrakanite (Na₂SO₄ · MgSO₄ · 4H₂O). During the summer it is covered with an 8-cm crust of these salts, with halite (NaCl) and epsomite (MgSO₄ · 7H₂O) crystallizing late in the summer (Bustillo *et al.*, 1978). Large amounts of astrakanite are formed on the (0.7 km² area) *Quero* playa-lake's surface during the summer. It is produced by the evaporation of lake brine to form a concentrated sodium sulfate solution, which then reacts with the previously deposited epsomite (Ordonez *et al.*, 1991).

There are also many high-sodium-sulfate springs in the valley, including at *Carcaballana*, *Carabana*, *Espartinas*, *Fuente de la Capa Negra* (Viciamadrid), *Loeches*, and *Valdilecha*, as well as under the *Fuentiduena de Tajo* and the city of *Madrid* (Ordonez and Garcia del Cura, 1992, 1994). Both small amounts of sodium sulfate and epsomite have been obtained from some of these springs since the Roman times by winter crystallization.

Ebro Basin

There are likewise a number of sodium sulfate lakes along the *Ebro Valley* in north central Spain, and a small amount of product has been recovered from some of them for the pharmaceutical industry. An example of such lakes is *La Salada* near Fuentes de Ebro (Zaragoza province). The lake contains deposits of thenardite and astrakanite, and on its shores glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$) has been identified. In the Bujaraloz-Alcaniz area of Zaragoza and Teruel provinces there are also many lakes, such as *La Playa*, in which some thenardite, glauberite, and astrakanite have been noted. Other sodium sulfate lakes, which can have salt contents of over 100 g/liter, include *El Camaron*, *Gullar* (3 km south of La Playa), *El Pez* (5 km from Guallar), *Pinto*, and *El Rebollon*. The Guallar playa has been studied for its magnesite (MgCO_3) content, with the conclusion being that residual high-magnesium brines either converted calcite (CaCO_3) to magnesite, or precipitated it directly from the high CO_2 created by decaying organic matter (Pueyo Mur and Ingles, 1987; Pueyo Mur, 1980; Ordóñez *et al.*, 1982; Mingarro *et al.*, 1979).

Other Areas

There are a number of other lakes and springs in Spain with a high sulfate content, such as in the *La Mancha* district of central Spain where there are more than 25 small saline lakes (average winter-flooded area 0.5 km^2) with a high sulfate and magnesium content, as seen in Table 3.14. No permanent soluble sulfate deposits have been reported, but during the summer efflorescence of thenardite, astrakanite, and perhaps glauberite form, and in the winter mirabilite crystallizes. All of the salts appear to redissolve in the spring when the playas are again flooded (Sanchez-Moral

Table 3.14
Examples of Brine Analyses of Spanish Sodium Sulfate Lakes

	SO_4	Cl	HCO_3^d	Na	Mg	Ca^d	K^d	Total
Quero Lake (wt%) ^a								
Spring	4.08	2.83	—	1.01	1.41	75	384	9.37
Summer	14.68	5.72	—	3.12	3.68	77	1210	27.33
Interstital	4.68	11.30	—	1.68	4.24	109	1550	22.06
Laguna de Tirez (wt %) ^b								
Spring	9.20	2.18	349	5.39	3.57	87	2060	20.70
Lakes Marcen, Almuniente (wt% of total salts) ^c								
Winter	15.2	34.2	0.6	46.6	2.4	1.0	—	100.0

^aMoral *et al.* (1994). La Mancha area.

^bDe la Pena *et al.* (1982). La Mancha area.

^cVizcayno *et al.* (1995). Flumen-Monegros District.

^dppm.

et al., 1998; Moral *et al.*, 1994; Ordonez *et al.*, 1994; De la Pena *et al.*, 1982). In the Flumen-Monegros district of northeast Spain there are also a number of sodium sulfate lakes with a lesser magnesium content. They do not contain soluble sulfate deposits, but do form sulfate crusts in the summer and winter. Both astrakanite (radiating prismatic and foliated rosette crystals) and burkeite ($2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$, platelike crystals, sometimes in spheroidal associations) have been reported, with the latter forming by capillary evaporation in the surface crust (Lopez *et al.*, 1996a,b; Vizcayno *et al.*, 1995; Augue *et al.*, 1995, 1994; Garces *et al.*, 1991; Mingarro *et al.*, 1981).

TURKEY

Acigol Lake

Several lakes and playas in Turkey are operated for commercial sodium sulfate production, the largest of which is Acigol Lake, with four operators in 1993. The lake has an area in the spring of 100 km^2 and a late summer area of 35 km^2 , with a maximum depth of 1.63 m (Fig. 3.30). It lies in a closed basin at the junction of Afyon, Burdur, and Denizli provinces, about 60 km east of the city of Denizli. Its altitude is 836 m, its annual rainfall 397 mm/yr, its summers hot (average 24.4°C) and dry (with the greatest evaporation in May and June; the total is 754 mm/yr), and its winters snowy and cold (an average of 3.3°C). The average temperature is 13.3°C . The lake is primarily fed by high-sulfate springs issuing from a fault line on its south side, with its surface drainage water (estimated as 14% of the rainfall) having passed over predominately marine limestone, sandstone, and mudstone, as well as some lacustrine rocks. A NW–SE ridge in the lake's sediments partially divides the lake into two subbasins, with the southern half the deepest. The lake is estimated to contain a certain 12.5 million mt of sodium sulfate in the surface and subsurface brine (there is no solid deposit), with probable reserves of 70 million mt, and possible reserves of 82 million mt. The differences in the estimates are based on various porosity, brine concentration-with-depth, and volume estimates for the lake's sediments, and each assumes an ability to economically and completely recover the interstitial brine.

The average analysis of 19 samples from the lake's brine (taken at a temperature of 20.4°C) and sediments are shown in Table 3.15, indicating a fairly high ratio of sodium sulfate to sodium chloride, and only modest amounts of other salts. However, the brine has a surprisingly high pH with no alkaline ions indicated in the analysis (i.e., CO_3 or B_4O_7 ; 322 ppm B noted in the text, 2–4 ppm B in the table). The springwater analysis is said to be similar, although much more dilute, and with higher Ca and Mg. Some nearby hot springs (at Beylerli; $37\text{--}40^\circ\text{C}$) had a total salts content of 1791 mg/liter, a flow rate of 20 liter/s, high levels of calcium and sulfate, and more magnesium than in the colder springs. Water in deep wells near the lake had a pH of 7.1–8.5.

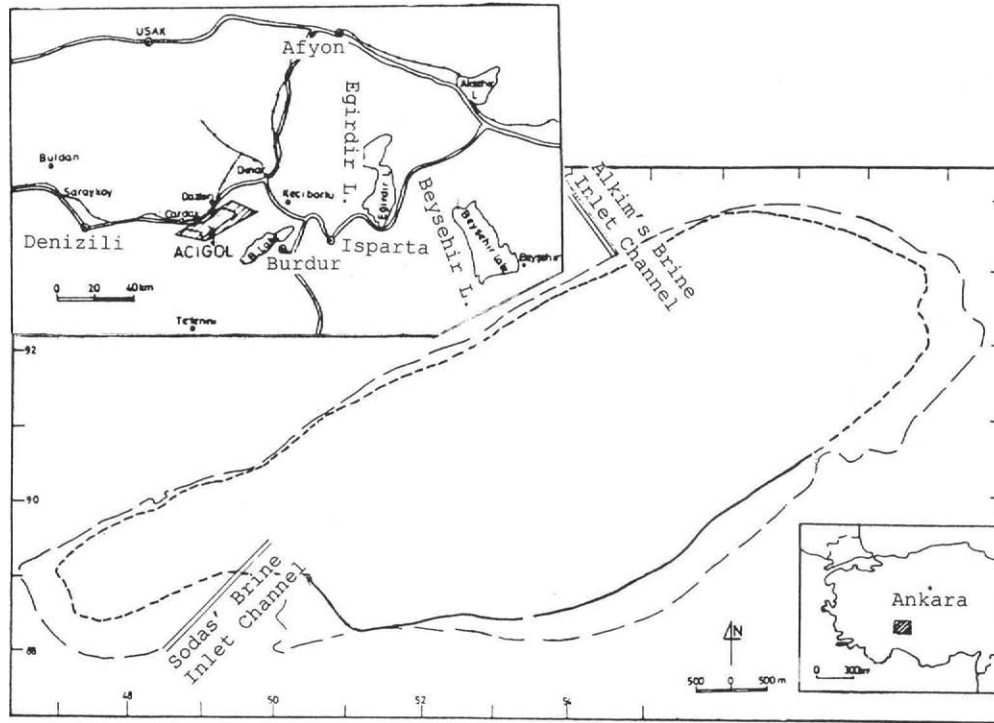


Figure 3.30 Acıgöl Lake, Turkey, and the location of two of its plants. (From Icozu and Calakpkulu, 1993.)

Table 3.15
Typical Analyses of the Brine in Turkish Sodium Sulfate Lakes (wt%) (Gundogan and Helvaci, 1996)

	Na	Mg	K	Ca	SO ₄	Cl	CO ₃ ^c	TDS	Density (g/cm ³)	pH
Acigol Lake ^a	5.45	0.42	0.17	0.06	4.89	6.11	0.01	17.11	1.152	8.0
Bolluk Lake (7-15-93)	1.75	0.86	0.25	0.07	2.73	3.43	0.07	9.16	1.085	8.5
Well No. 1 ^b (5-10-85)	325	227	25	662	1630	496	1140	4510	1.015	6.2
Tersakan Lake (7-15-93)	1.86	0.70	0.22	0.09	2.27	3.43	0.05	8.62	1.078	8.2
Artesian Well ^b (4-14-86)	1460	1030	664	428	4350	3120	546	11600	1.027	7.1
S. Bayhan ^b (10-1-84)	328	193	22	656	1760	490	796	4240	1.011	6.4
Tuz Golu	9.68	0.27	0.12	0.07	0.67	15.7	0.02	26.5	1.24	7.2

^aIcozu and Calakpkulu (1993). Also 2–4 ppm B.

^bppm.

^cAll of the HCO₃ has been reported as CO₃.

The lake's sediments are yellowish green to blackish blue plastic clay, with abundant gypsum crystals, gastropod fossils, and sulfur nodules. The clay constituents are quartz, calcite, dolomite, bassanite $[(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}]$, aragonite, and considerable organic matter. Both sulfur-reducing and sulfur-oxidizing bacteria are present in different areas of the underlying mud. Mirabilite $(\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O})$ crystallizes from the lake's brine each winter and redissolves the following spring (Icozu and Calakpkulu, 1993).

Bolluk Lake and Tersakan Lake

These two small lakes also have commercial sodium sulfate production ($\sim 10,000$ t/yr each of a crude product) and are operated by the same company that has two facilities at Acigol Lake (Alkim). They are close together in the Tuz Golu (a much larger high-sodium-chloride lake) drainage basin, and about 9 km south or 7 km ESE of Cihanbeyli, respectively (Fig. 3.31). This area is in central Anatolia, about 150 km

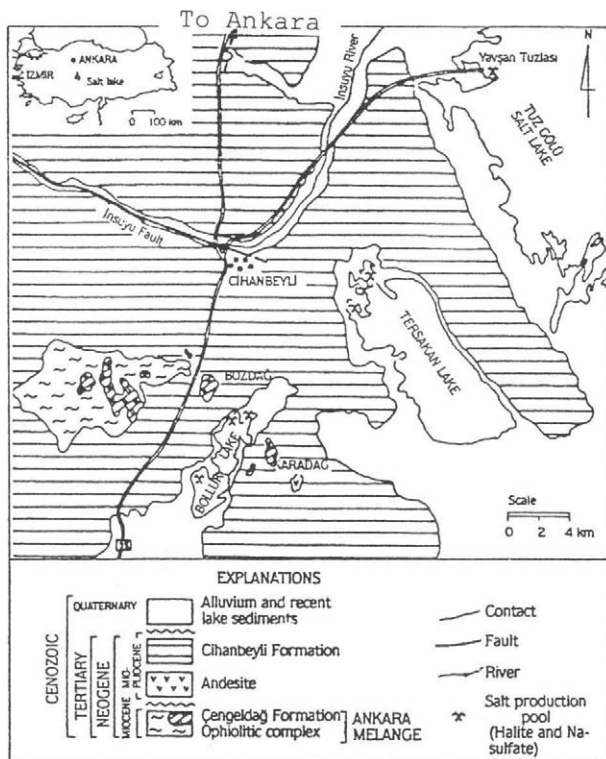


Figure 3.31 Location map and geologic formations near Bolluk and Tersakan Lakes, Turkey. (From Gundogan and Helvaci, 1996, courtesy of *Turkish Journal of Earth Sciences*.)

south of Ankara, and has a cold (average 11–14°C), dry (293 mm/yr rainfall; 59% average relative humidity) climate, with temperatures exceeding 20°C in July and August. Bolluk Lake has an area of 20 km², Tersakan Lake 56 km², and both are fed almost entirely by high-sulfate and -chloride, medium-magnesium, calcium bicarbonate-saturated springs (Table 3.15), which replenish the lakes' annual sodium sulfate production. The small amount of runoff water that enters the lakes flows over predominately gypsiferous mudstone in the west, and oolitic limestone on the east, with some areas of andesite and gypsum-bearing dolomitic lake muds. There are 63 springs in and to the northeast of Bolluk Lake, with travertine cones ranging from 3 to 200 m in diameter and 1 to 30 m in height. The springs rise from a volcanic fault line parallel to the lake, and a few of the cones are still forming. Their runoff supplies high sulfate-chloride-bicarbonate water to the lake and has formed bottom sediments of aragonite, calcite, dolomite, and magnesite, with dolomite predominating. Gypsum crystals are also very common in the lake muds, and some anhydrite is present.

As the lake waters evaporate during the summer they eventually crystallize halite and some thenardite (Na₂SO₄) and astrakanite (Na₂SO₄ · MgSO₄ · 4H₂O). Mirabilite forms extensively during the winter (Fig. 3.32), but all of the salts dissolve in the spring and there are no permanent salt deposits in the lakes. All waste brines and wash waters from the plant and ponds are also returned to the lake, making it appear that considerable seepage occurs to allow the entering sodium chloride, magnesium sulfate, and other higher-solubility salts to escape. Their concentration has not increased in the lake brine over the many years of operation, and they do not appreciably leave with the product. A similar situation occurs with Acigol Lake. Table 3.15 lists typical lake and adjacent well water analyses (Gundogan and Helvaci, 1996).

Some areas of Turkey also contain high-sodium-sulfate soils (Van Doesburg *et al.*, 1982; Vergouwen, 1981; Driessen and Schoorl, 1973), and various general articles have been written that mention the Turkish sodium sulfate operations (e.g., Garcia Saez, 1993; Karayaziri, 1988).

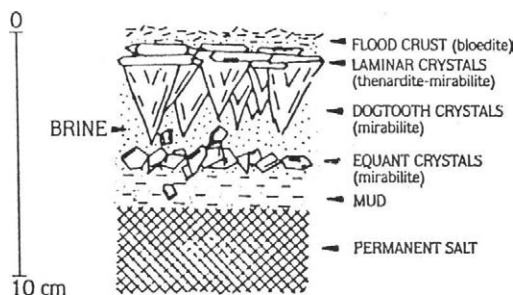


Figure 3.32 Typical mirabilite crystal structure in Bolluk Lake. (From Gundogan and Helvaci, 1996, courtesy of *Turkish Journal of Earth Sciences*.)

Table 3.16
Sodium Sulfate Analyses from Soda and Dale Lakes, California (wt%)

	Na ₂ SO ₄	NaCl	MgO	CaO	K ₂ O	Insol.	TDS
Soda Lake							
Surface crust ^{a,c}	87.74	9.39	1.68	0.46	0.28	0.45	—
Surface crust ^b	98.65	0.47	0.43	—	—	0.45	—
Mirabilite ^b	99.26	0.74	—	—	—	—	—
Product ^d	91.61	6.09	1.02	0.35	—	0.93	—
Brine ^d	9.08	14.09	1.88	0.05	—	—	25.10
Dale Lake brine ^e	6.72	21.99	0.05	0.08	—	—	28.84

^aCole (1926).

^bArnold and Johnson (1909).

^cGale (1914) stated that the brine varied from 26.39 to 30.19% salts, with 0.54–1.20% KCl, and the surface crust contained 88.12–89.66% soluble salts, with 0.09–0.13% KCl.

^dGarrett (1966). Also 200 ppm CO₃, 9 B, 0.4 Li, and $\rho = 1.192$.

^eGarrett (1966). Also 86 ppm B and 330 CO₃.

The Carriso Plain is a block faulted basin between the Caliente and Temblor ranges, with the San Andreas fault running along one side. This has caused considerable faulting and folding (some quite recent) in the basin. The lake surface is covered with a 2- to 30-cm crust (average about 25 cm) that is largely sodium sulfate, with occasional zones that are over 1.8 m thick. The lake floods with water during the winter and dries in the summer and fall to form the surface crust, with the brine level remaining just below the surface. The initial estimated reserves were over 1 million t of Na₂SO₄, not including the brine that permeates the salts, and the salts and brine in the mud beneath the lake's surface, but since that time both leaching and seepage have taken place. Typical analyses of the surface salts are given in Table 3.16 (Arnold and Johnson, 1909).

Gale (1914) noted that there was considerable astrakanite (Na₂SO₄·MgSO₄·4H₂O) in the lake's mud, and that the brine was relatively high in potassium. The digging of numerous shallow pits did not encounter beds of mirabilite (Na₂SO₄·10H₂O), and deeper, more extensive drilling has never been done on the lake. Eadie (1966) reported that the astrakanite was mainly found toward the center of the lake (such as 0.2 km offshore) and occurred as scattered crystals in the black mud 1.2–1.5 m deep under the surface mirabilite layer. The astrakanite crystals varied in size from microscopic to over 23 cm long and were associated with some mirabilite, thenardite (Na₂SO₄), and glauberite (Na₂SO₄·CaSO₄). They were blackish in color (from occluded organic matter) and had a perfect monoclinic habit.

There was intermittent commercial production of sodium sulfate for a few years from 1908 to 1915, and again in 1963, but apparently the output was never very great. The surface crust was initially leached in place, the brine collected and sent to solar ponds, and thenardite then crystallized (or mirabilite deposited and

dehydrated) in the ponds. The sodium sulfate was harvested and sold as about a 92% Na_2SO_4 product (Table 3.16; Ver Planck, 1962). In the later operation an attempt was also made to leach the salts from the near-surface mud (Eadie, 1966).

Dale Lake

Dale Lake is located further south in the Mojave Desert, in the south center of the state about 32 km east of Twenty-nine Palms (Fig. 3.34). It is roughly 8×4.8 km in size, with a surface area of 10–13 km², and contains lenticular beds of thenardite and halite. The mixed salt beds alternate with layers of salty shale, with the pure salts being up to 31 m thick and varying considerably. The beds are not laterally continuous, but in one area a 9.1-m bed begins at a depth of 6–12 m, and a second 30.5-m bed starts at 36.6 m depth. Other beds extend to a depth of 91 m. Some layers consist of pure halite or thenardite, but the average for the lake is a mixture containing 60% Na_2SO_4 , 30% NaCl, and 10% insolubles. The lake sediments are quite permeable and filled with a high-salt, medium-sulfate brine, averaging about 7.5–8% Na_2SO_4 and 20–22% NaCl (Table 3.16). The estimated Na_2SO_4 reserves are 11 million (Wright *et al.*, 1953; Majmundar, 1985).

Initially open pit mining was attempted on the thenardite–halite beds, but problems with brine inflow and an inability to leach enough of the halite from the product prevented the operation from being successful. Later, in the late 1950s, one of the procedures utilized at Searles Lake (Anon., 1962) was copied to first form glauber

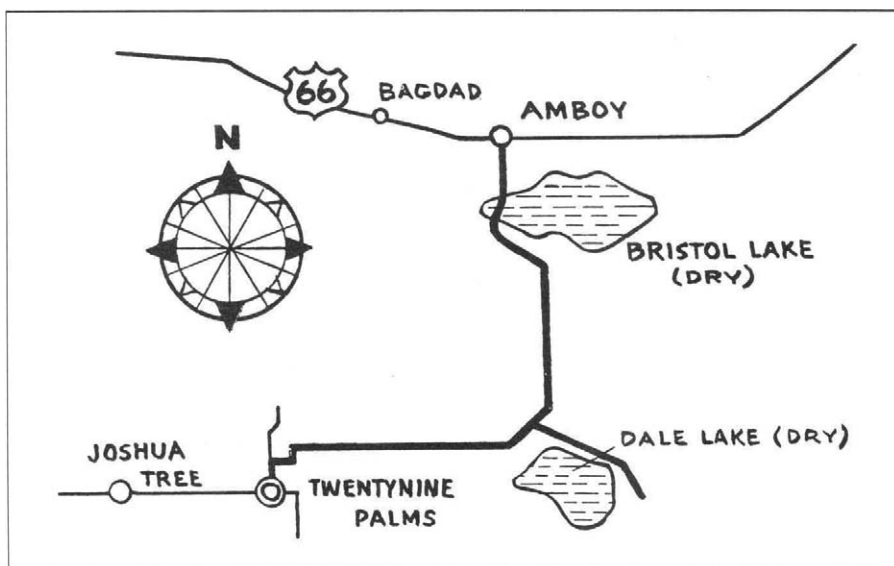


Figure 3.34 Location map of Dale and Bristol Lakes, California. (From Garrett, 1966)



Figure 3.35 The winter spraying of Searles Lake brine. (From Anon., 1962, by permission of *Chemical Week*.)

salt from the brine. Brine was sprayed into the air in the winter whenever the temperature was less than about 5°C , and a large mound of mirabilite eventually accumulated on the surface (Fig. 3.35). This was harvested during the year, dehydrated, and sold as a medium-purity product. In the mid-1960s a large ($>\$1$ million) plant was built to produce 50,000 t/yr of sodium sulfate by this process. It employed 12 94-m-deep wells that were each capable of pumping 204 gpm at a 27 m head of a 1.22 g/cm^3 brine. In normal practice only 10 wells were used at a time, each pumping 157–189 gpm with an average 9.4-m drawdown. The glauber salt from the pile was washed and drained in the plant, with the slimes being settled and removed in a 30 m diameter thickener, and then discarded. The glauber salt was dehydrated in a 2.4×18 m rotary dryer and cooled in a 0.9×9 m rotary cooler. The plant had an extensive infrastructure because of its remote desert location, but it only operated for about 6 months before being sold in bankruptcy (Garrett, 1966).

Danby Lake

A few carloads of sodium sulfate have also been obtained from the nearby Danby Lake that contained sodium sulfate in its brine and sediments. The lake is about $16 \times 3.2\text{--}4.8$ km in size and contains a 0.3–3 m thick bed of halite and other salts on or under the surface over a $21\text{--}41\text{ km}^2$ area. Brine occurs within 1.2–1.5 m from the surface (Wright *et al.*, 1953), and in a nonsalt area ponds were constructed, flooded, and plowed to leach the mud's content of small mushroom-shaped mirabilite crystals. This brine was then evaporated, and mirabilite was crystallized, dehydrated, harvested, and shipped without further processing.

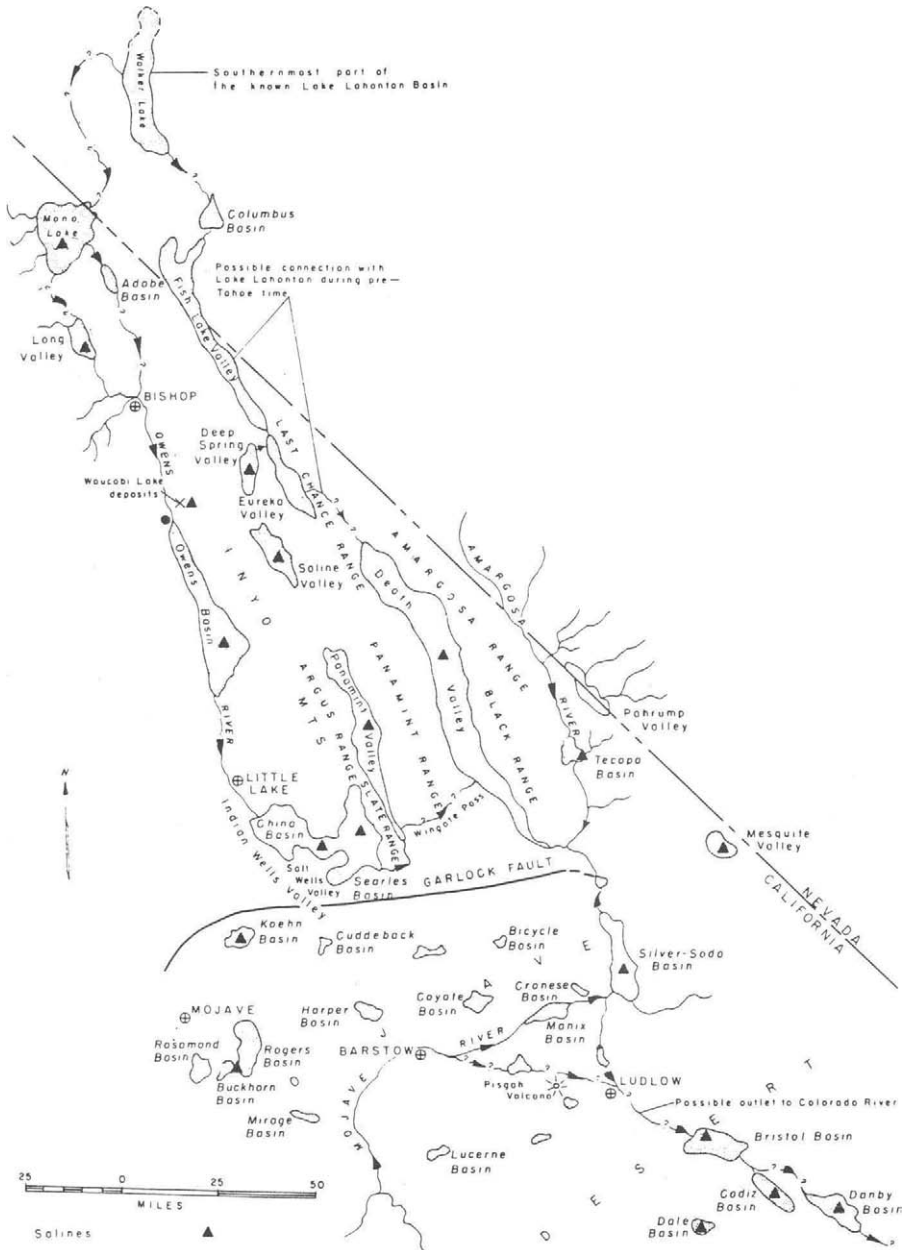


Figure 3.36 Dry lakes and their probable drainage paths in California's southeastern deserts. (From Garrett, 1992.)

Searles Lake

This lake contains one of the largest sodium sulfate deposits in the world (369 million mt Na_2SO_4 , 65 million mt K_2SO_4 ; along with comparably large amounts of potash, borax, soda ash, halite, and other salts; Fairchild *et al.*, 1997) and has produced more sodium sulfate (Anon, 1951a) than any other deposit. It is located in the northwest corner of the Mojave Desert, 200 km north-northeast of Los Angeles (Fig. 3.36). Its block-faulted valley has a drainage area of about 1600 km² and is

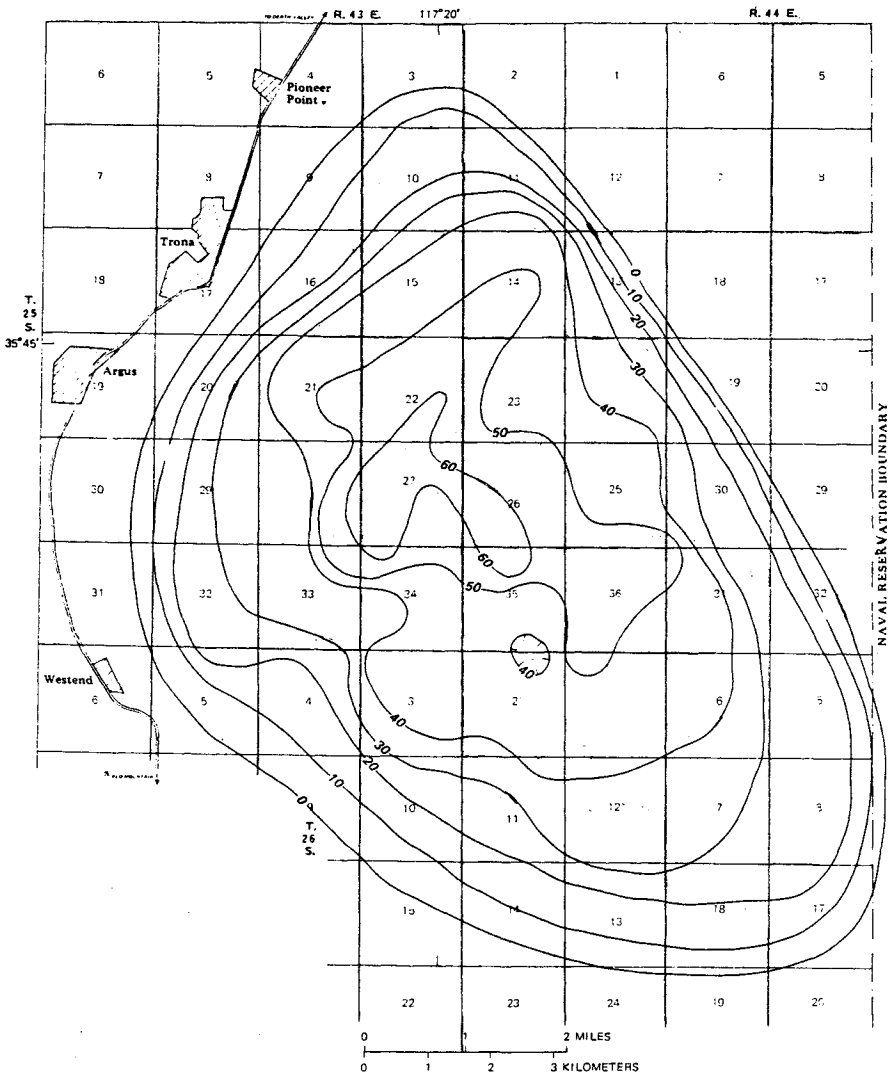


Figure 3.37 Thickness map of Searles Lake's upper salt body (ft). From Smith, 1979.

Table 3.17
Typical Brine Analyses in the
Upper and Lower Salts at
Searles Lake^a

	Upper salt (%)	Lower salt (%)
KCl	5.08	2.94
Na ₂ CO ₃	4.80	6.78
Na ₂ B ₄ O ₇	1.63	1.96
Na ₂ SO ₄	6.75	6.56
NaCl	16.06	15.51
Na ₂ S	0.08	0.38
Li ₂	0.015	0.006
KBr	0.12	0.08
WO ₃	0.007	0.004
I ₂	0.003	0.002
P ₂ O ₅	0.070	0.044
F	0.002	0.002

^aFrom Garrett, 1992.

32 × 16 km in size, and the lake has a nearly elliptical 16 × 10 km surface and deposit (Fig. 3.37). Its area is 100 km², of which 37 km² consists of massive halite that extends from the surface to the upper mixed crystal mass. Its altitude is 492 m, the average rainfall in the valley is 96 mm/yr, and the temperatures vary from -7 to 49°C, with the mean being 19–21°C. The lake is normally dry, but during some winters the surface floods with a few centimeters of water that evaporates rapidly. The subsurface brine that fills the lake and salt beds is never more than 1 m from the surface.

The Searles Lake deposit has two massive brine-filled (Table 3.17) mixed salt beds formed 3500–40,000 years ago, and a much older and deeper trona-nahcolite-halite (Na₂CO₃ · NaHCO₃ · 2H₂O–NaHCO₃–NaCl) with lesser amounts of burkeite–thenardite (2Na₂SO₄ · Na₂CO₃–Na₂SO₄) deposit. The upper deposits' primary mineral source was a group of still-flowing hot springs in the Owens Valley area (Garrett and Carpenter, 1959), along with some salts from drainage water. Searles Lake was the final basin that received waters from the Owens River (and its hot springs), flushed by ice-age storms 190–270 km to the north (Fig. 3.36). When it was filled 180 m (600 ft) above its present level, its stratified freshwater overflowed into the Panamint Valley, and then Death Valley (Smith and Pratt, 1957). The lake is unique among the world's large sodium sulfate deposits in containing a mixture of sodium sulfate minerals (Table 3.18) with many other salts, and a high-Na₂SO₄ brine.

During the first 7900 yr that the river's and hot springs' water accumulated in the lake, only mud was deposited, but in the next 8500 yr complex soluble salt beds, separated by comparatively thin mud seams, were crystallized to form the 12-m "Lower Structure," or lower salt body. Water next accumulated for another 13,500 yr,

Table 3.18

Some of the Soluble Sulfate Minerals Found in the Searles Lake Deposit^a

Mineral	Composition
Burkeite	$2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$
Galeite	$\text{Na}_2\text{SO}_4 \cdot \text{Na}(\text{F}, \text{Cl})$
Glaserite (aphthitalite)	$\text{K}_3\text{Na}(\text{SO}_4)_2$
Hanksite	$9\text{Na}_2\text{SO}_4 \cdot 2\text{Na}_2\text{CO}_3 \cdot \text{KCl}$
Mirabilite (glauber salt)	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
Schairerite	$\text{Na}_2\text{SO}_4 \cdot \text{Na}(\text{Cl}, \text{F})$
Sulfohalite	$2\text{Na}_2\text{SO}_4 \cdot \text{NaCl} \cdot \text{NaF}$
Thenardite (sodium sulfate or salt cake)	Na_2SO_4
Tychite	$\text{Na}_2\text{SO}_4 \cdot 2\text{Na}_2\text{CO}_3 \cdot \text{MgCO}_3$

^aFrom Garrett, 1992.

laying down 4 m of “parting mud.” This was followed by 7000 yr when the 15-m “Upper Structure,” or upper salt, was crystallized (Fig 3.37, 3.38), which ended 3500 yr ago. Since that time the upper salts have been covered by halite in the central area, and mud in the outlying zones. The Upper and Lower Salts have a 35% void volume, originally filled by the lake’s end liquor (Smith, 1979). Brine has been pumped to processing plants since 1916, with the original “mother liquor” now depleted, and a weaker equilibrium brine formed by leaching the salts is the brine presently being recovered (Anon., 1951a).

It appears that as the initial salts crystallized in the lake by both winter cooling and summer evaporation, they compacted in a normal manner to a fairly low porosity, and then were capped by either clay or halite. Over the intervening years, the mirabilite that was present slowly “melted” and converted to thenardite at the mean average ground temperature of 19–21°C (the NaCl – Na_2SO_4 – $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ – H_2O transition temperature is 18°C), followed by a similar dehydration of natron and some of the borax. These transformations resulted in a high void volume, since the other crystals provided a strong noncollapsing mass for these shallow beds. It also allowed convection currents to “mix” the solution, dissolving and recrystallizing the original salts into the more complex true equilibrium minerals such as burkeite ($2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$), glaserite ($3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$), hanksite ($9\text{Na}_2\text{SO}_4 \cdot 2\text{Na}_2\text{CO}_3 \cdot \text{KCl}$), and many sparingly soluble carbonate, borate, potassium, etc., compounds. This slow conversion is borne out by their often large and perfect crystal size and shape (e.g., hanksite crystals 10–15 cm in diameter are common). Many of the minerals in the lake have been found only in a few other places.

The Lower Salt is of middle Wisconsin age and consists of a series of alternating layers of mud and crystals about 1 m thick. Trona is the dominant mineral in beds 1–3 and 6–7; trona and burkeite in 4; and halite, trona, and burkeite in 5. Lesser amounts of northupite ($\text{Na}_2\text{CO}_3 \cdot \text{MgCO}_3 \cdot \text{NaCl}$), thenardite, hanksite, and borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) occur in all zones, and still smaller quantities of nahcolite,

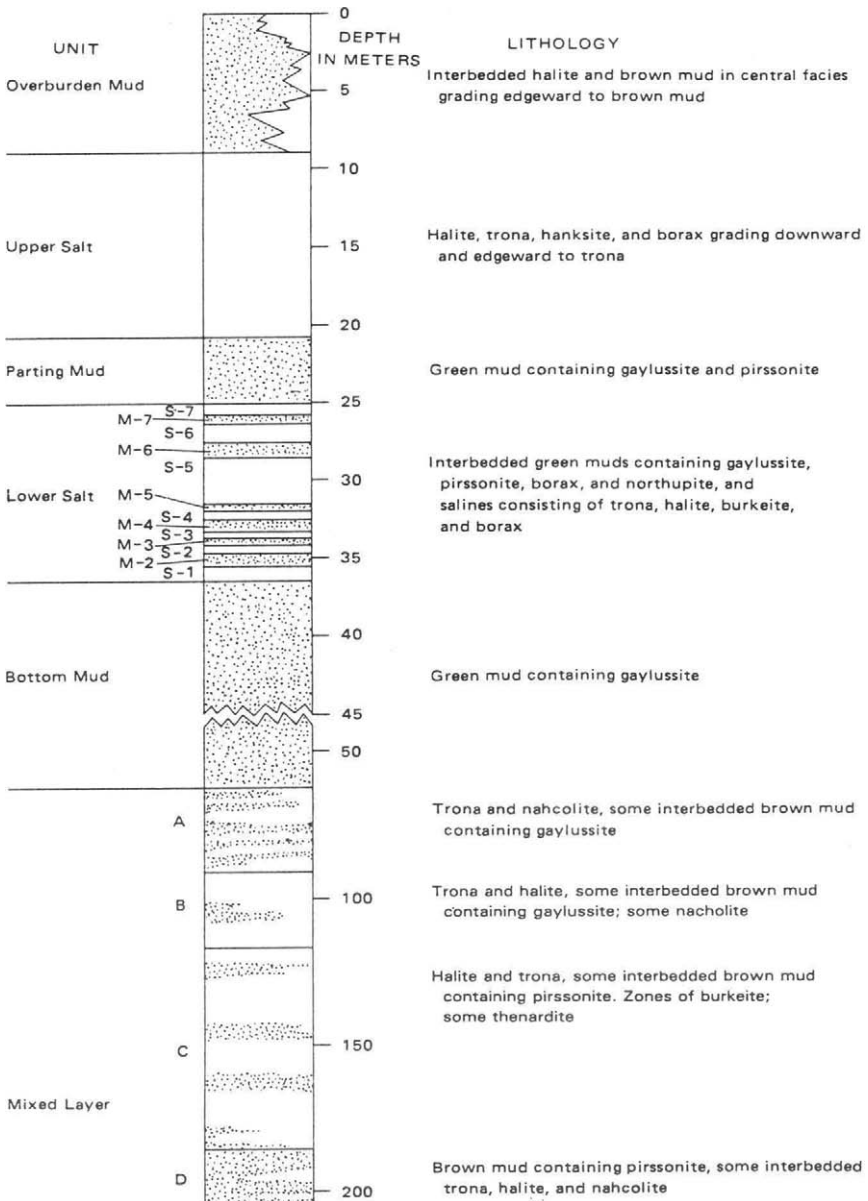


Figure 3.38 Typical stratigraphy of the three saline zones in Searles Lake. (From Smith, 1979.)

Table 3.19
 Typical Analysis of the C Unit in Searles
 Lake's Lowest, or Mixed Layer^a

Bed (m)	% soluble salts	Percentage of total salts			
		Trona	Nahcolite	Burkeite	Halite
0.30	86.4	69.0	3.3	7.2	20.5
0.91	98.2	0	1.4	18.6	80.0
1.10	82.3	83.3	3.2	4.3	9.2

^aFrom Garrett, 1992.

sulfohalite ($2\text{Na}_2\text{SO}_4 \cdot \text{NaCl} \cdot \text{NaF}$), and tychite ($\text{Na}_2\text{SO}_4 \cdot 2\text{Na}_2\text{CO}_3 \cdot \text{MgCO}_3$) are found locally. Most of the saline mineral beds contain thin layers of mud, and some of these include a little gaylussite ($\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 5\text{H}_2\text{O}$) or pirssonite ($\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 2\text{H}_2\text{O}$). The mud is composed of silt to clay-sized carbonates, silicates, and organics.

The 3.7–4.3 m (12–14 ft) Parting Mud separates the Upper and Lower Salts and contains crystals of gaylussite, pirssonite, and a little borax, along with its dark-green to black silicates and organic debris. In its upper one to two-thirds thin laminae of white aragonite (CaCO_3) are numerous. Its outer limits extend for 1000 km², well beyond the salt areas, and form scattered outcrops around the basin. The 114 km² Upper Salt (Fig. 3.38) is 15 m thick near its center and is lens-shaped. Its most abundant minerals are halite, trona, and hanksite, with smaller quantities of borax, burkeite, pirssonite, thenardite, glaserite, and sulfohalite. Compared with the Lower Salt it contains more halite and hanksite, about the same amount of borax, less thenardite, trona, and burkeite, and no significant mud layers. The brine is higher in K, SO_4 , and Cl, and lower in CO_3 and B_4O_7 (Haines, 1959; Smith and Pratt, 1957; Smith, 1979).

The deeper (67–267 m), older (120,000–1,000,000 yr) “Mixed Layer” salts in Searles Lake contain a lower percentage of sodium sulfate. The upper A and B “units” are mostly trona and nahcolite, or trona and halite, respectively, but the C unit contains more burkeite and some thenardite (Table 3.19). Most of the individual beds consist of a mixture of minerals, but there are some of pure trona or halite. Their thickness varies up to 1–3 m, and there is considerable clay between them (Garrett, 1992).

Owens Lake

Owens Lake is the first of the chain of lakes on the eastern slopes of the Sierra Nevada Mountains that overflowed during the recent ice ages to allow most of their soluble salts to deposit in Searles Lake (Fig. 3.36). The lake is now usually dry and only contains surface and near-surface salts, as well as the interstitial brine in these

Table 3.20
Soluble Salts Content of Owens Lake (wt%)^a

	1912 brine composition			Present composition			
	Brine	Dry basis	Million mt	Brine	Solids	Total	Million mt ^b
Na ₂ SO ₄	4.4	43.9	64.5	4.5	2.6	11.9	9.6
Na ₂ CO ₃	—	—	—	8.9	—	—	—
NaHCO ₃	3.5	35.0	53.6	0.2	41.5	47.8	38.6
NaCl	0.7	6.1	10.1	18.0	25.0	27.0	21.8
KCl	1.6	15.0	24.3	—	12.4	13.3	10.7
Na ₂ B ₄ O ₇	0.5	—	6.7	—	—	—	—
Insol.	0.3	—	4.1	—	9.1	—	—
Water	89.0	0	—	68.4	9.4	—	—
Total	—	—	163.3	—	—	—	80.7

^aFrom Garrett, 1992.

^bThe missing salts are presumably in the (now heavier) interstitial brine (or as crystals) in the underlying mud.

salts. There are 9.6 million t of Na₂SO₄ present, and the deposit is about 3500 years old, the same as the youngest upper structure salts in Searles Lake. Its valley is 160 km long and 24 km wide, formed by block-faulting of the Sierra Nevada mountains to the west and the Inyo Range to the east. Present-day steam fumaroles at Hot Creek and Coso Hot Springs still contain unusual amounts of sulfate, boron, potassium, carbonates, etc., and flow into the Owens River. The Owens Valley's elevation is 1081 m, and until 1917 the lake was a moderately deep, fairly dilute alkaline body (Table 3.20), with an area of about 259 km² (100 mi²). It supported steamboat traffic to bring ore from mines on its eastern side to the railroad at its southwest corner. However, Los Angeles purchased the water rights feeding the Owens River, and when an aqueduct was opened in 1917 the entire flow of the Owens River was diverted. The lake began to dry up, and by 1922 it was almost totally dry. It now covers 87.5 km², and in the summer contains a slushy mixture of 35 vol% brine and 65 vol% solids (70.4 wt%), averaging 0.8 m (maximum, 3 m) in thickness. Trona is the dominant salt, with lesser amounts of mirabilite, burkeite, borax, natron (Na₂CO₃ · 10H₂O), and thermonatrite (Na₂CO₃ · H₂O). In the winters considerable mirabilite, natron, and borax crystallizes, but they "melt" in their own water of crystallization and/or are dehydrated (by NaCl) in the hot summer months. Halite, trona, thenardite, and burkeite form during the summer. The brine has considerable dissolved organic matter ("humates"), and there is some sulfate-reducing bacterial action. There were several soda ash-borax plants on the lake from 1915 to 1958, but sodium sulfate has never been recovered. It has been speculated that the missing sodium sulfate from the 1912 estimate (64.5 mil.t) to the present (9.6 mil.t; Table 3.20) is due to seepage of heavier brine into the lake's sediments, which also liberated NaHCO₃ (Garrett, 1992).

Saline Valley

Saline Valley is a small valley surrounded by high mountain ranges 24 km northeast of Owens Lake (Fig. 3.36). In its center is a nearly circular 41 km² salt-covered (2–91 cm thick), brine-filled playa that in the past has supported commercial borax and later halite operations. Sulfur has also been mined in its southwestern mountains. As with many desert valleys, almost all of the water flowing into the playa is through alluvial fans, and the water composition varies considerably in each of the playa's four quadrants (see Garrett, 1992). This has resulted in considerable segregation of the mineral deposits in the playa, with one area containing considerable mirabilite and thenardite, surrounded by major amounts of glauberite. Figure 3.39 shows an estimate of the salts' distribution below the surface crust to a depth of 4.5 m.

High-carbonate/bicarbonate waters enter from the northeast and a narrow zone in the center of the west side, precipitating all of the calcium, and allowing sodium chloride and sodium sulfate to concentrate. Mirabilite and thenardite have crystallized prolifically in these zones, and even though not reported, astrakanite must also be present (because the carbonate-depleted waters still have a high magnesium content). High-calcium groundwater enters from the south and northwest, first crystallizing gypsum, and then reacting with the mirabilite, thenardite, and astrakanite. This has formed glauberite in the areas surrounding the two high-sodium-sulfate zones. The low point in the playa is to the southwest where a generally perennial lake about 2.6 km² in the area has formed a zone of quite pure and thick halite. Elsewhere in the playa there is a clayey-salt crust formed by the predominately capillary evaporation that occurs with the high-sulfate underlying brine, and which contains a mixture of minerals (including thenardite, mirabilite, and glauberite). In the northeast corner this crust had a high borax-carbonate content (from entering geothermal springs), which was recovered during the period around 1900. In the northeast and central west areas there are thin beds of mirabilite (formed during the winters), thenardite (up to 1.2 m thick), and a high concentration of these minerals (mainly thenardite) disseminated in the mud. At the outer edges of these zones and in the west-center, glauberite is the dominant salt, usually disseminated in the mud, and at times amounting to 40% of the mixture. Its euhedral crystals are often 5–7 mm long and may occur in pockets of closely packed crystals (Hardie, 1968).

Deep Springs Valley

Deep Springs Valley is northeast of Owens Lake, and just north of Saline Valley (Fig. 3.36 and 3.40). It also contains a small high-sulfate-carbonate playa, about 13 km² in area, and with very recently deposited salts (1000 yr). Only a 7.6- to 30.5-cm thick laminated crust has formed, but beneath that is an interesting sequence of salts, as seen in Fig. 3.41. The upper layer is a mixture of all the salts in the underlying brine (resulting from capillary evaporation), but primarily halite or mixtures of trona and halite. Under the surface layer is a porous, flaky layer of massive, anhedral or tabular burkeite, usually with many inclusions, and occasionally surrounding thenardite crystals. Next there are uniform coarse-grained layers of

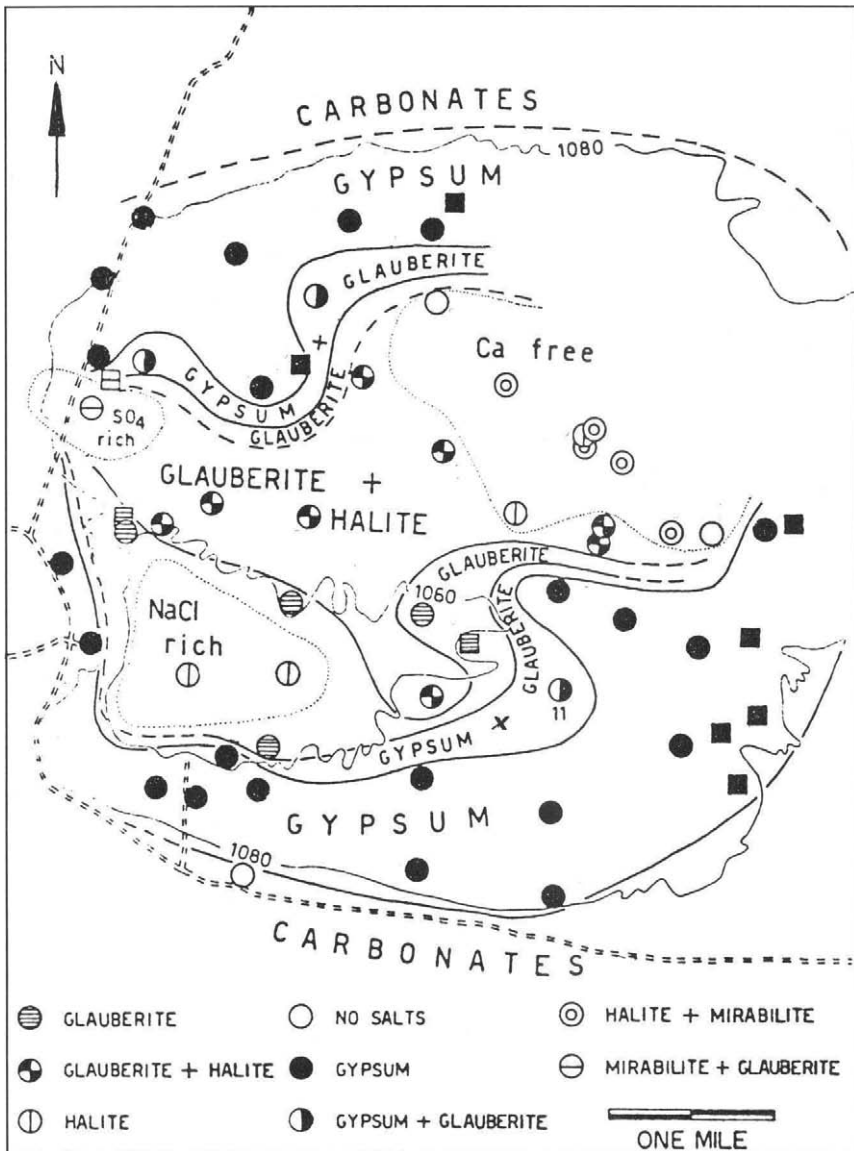


Figure 3.39 Distribution of minerals in Saline Valley, California. Squares indicate less prevalent. (Reprinted from *Geochim. Cosmochim. Acta*, Hardie, L.-A., "The Origin of Nonmarine Evaporite Deposit of Saline Valley, California," pp. 1270–1301, © 1968, with permission from Elsevier Science.)

massive anhedral thenardite up to 13 cm thick, usually comprising about 75% of this saline layer. Below that are irregular patches of thenardite clusters (generally pointing down, and mixed with some glaserite [$3K_2SO_4 \cdot Na_2SO_4$]). At the bottom some nahcolite has been reported, perhaps from CO_2 (from decaying vegetation)

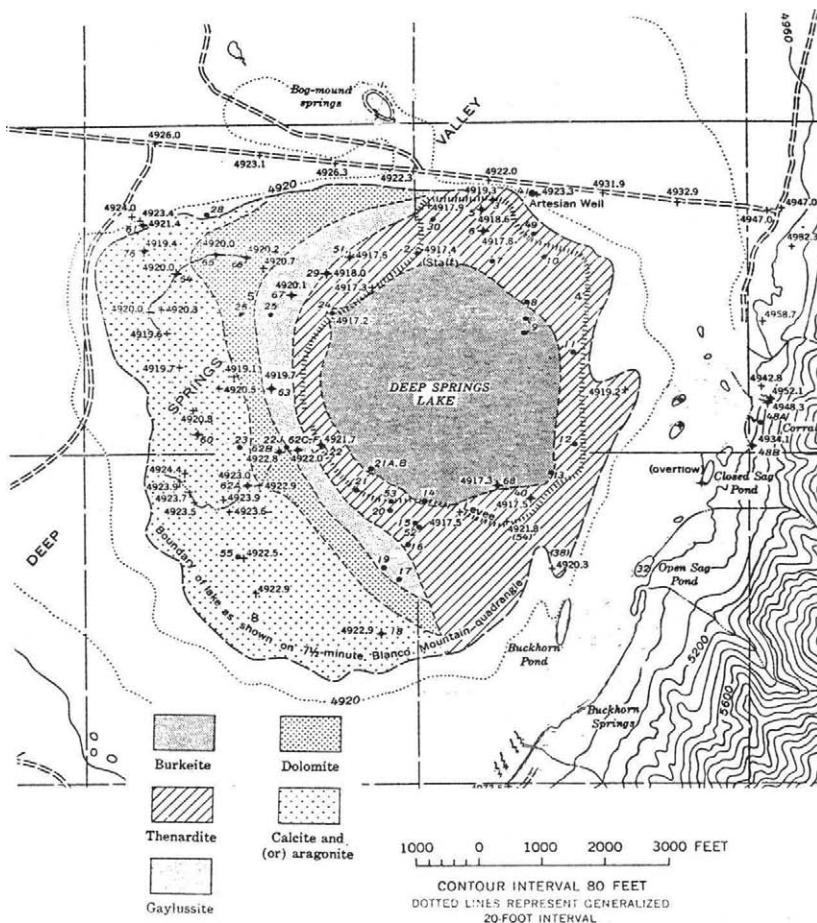


Figure 3.40 Distribution of minerals in Deep Springs Lake, California. (From Jones, 1965.)

reacting with the brine. There are also disseminated thenardite crystals in the mud flats surrounding the saline-covered playa (Jones, 1965).

Other Playas

There are many other occurrences of sodium sulfate minerals in California, and some of them are fairly large. One of the minor, less concentrated deposits that has been quite intensively studied is in *Death Valley*. In the northern and eastern edges of the Cottonball Basin thenardite is the dominant material in the surface crusts, formed by capillary evaporation of a near-surface high-sulfate groundwater. Similar deposits form in the area of the entering Amargosa River waters to the south of Death Valley. Glauberite is abundant in the sediments of the Badwater Basin to the

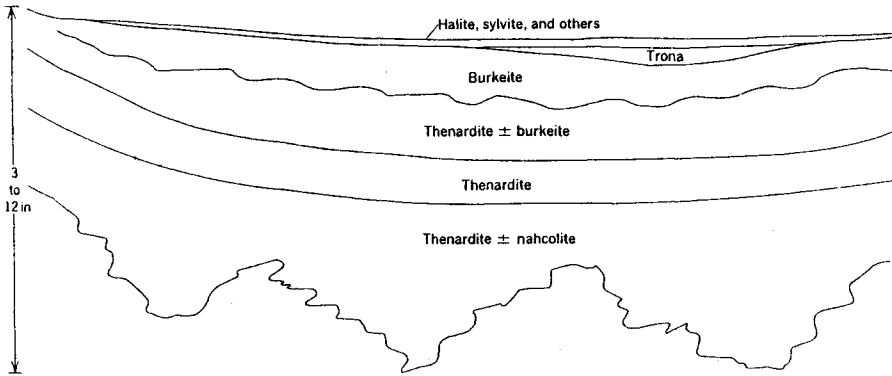


Figure 3.41 Distribution of minerals in the near-surface crust of Deep Springs Lake, California. (From Jones, 1965.)

north, formed by the high-calcium springs in that area (Crowley and Hook, 1996). Both glauberite and thenardite are common in core samples taken throughout the valley, with their abundance dependent upon the aridity and dominant water source in each area and period (Li *et al.*, 1997; Yang *et al.*, 1996). Other high-sodium sulfate playas have been reported, including *Borax Lake* (Garrett, 1998; Silliman, 1868), the *Black Basin* in the *Old Dad Mountains*, at *Emerson Lake* 97 km east of Victorville, and in the brines of *Mono Lake* (Smith, 1966; Ver Planck, 1956, 1962). No production has been reported from these playas.

Montana

Most of the sodium sulfate lakes in Montana are in its northeast corner and are a continuation of the extensive glacial lakes of the south-central Canadian prairie. (Fig. 3.6). They have not been drilled or thoroughly examined, but the few brine analyses that are available (Table 3.21) indicate that they are typical of the other lakes in this system. Some of the larger high-sodium-sulfate lakes are Big Lake (5.2 km² area), the Brush Lake area with seven lakes 8–130 ha (20–320 ac) in size, Kingsburt Lake (also called Alkali or Mallard Lake, 4.7 km²), Lost Lake (65 ha), and the Westby area with six lakes to the south and 10 lakes to the north (16–130 ha in size; Sahinen, 1956).

Nevada

Rhodes Marsh

There are a number of playas in Nevada with a high sodium sulfate content, with perhaps the largest, and the one from which the most sodium sulfate has been recovered being Rhodes Marsh. It is located near the southwest edge of the state, 14 km south of Mina, at an altitude of 134 cm and with a 515 km² drainage basin.

Table 3.21
Brine Analyses for Several Montana
Sodium Sulfate Lakes (wt%) (Sahinen, 1956)

	Na ₂ SO ₄	MgSO ₄	CaSO ₄ ^a	NaCl ^a	KCl ^a	K ₂ SO ₄ ^a	NaHCO ₃ ^a	CO ₃ /HCO ₃ ^a	TDS
Lost Lake	11.88	1.63	322	—	602	5620	—	354 ^b , 297 ^c	15.38
Westby South	8.33	—	—	—	906	904	1360	5520 ^d	9.06
Westby North	13.00	—	—	3150	3870	—	387	497 ^d	13.79

^appm.

^bMg(HCO₃)₂.

^cMgCO₃.

^dNa₂CO₃.

It has a nearly circular shape 4–4.8 km in diameter (4.8 km long and 2.4 km wide; Vanderburg, 1937), and with an area of 13–15.5 km². Most of its salts are porous and filled with brine, with the level varying from being flooded 5 cm or so in the winter (Williams, 1883) to not less than 1.2–1.5 m from the surface in the driest summers. The playa was successfully mined for both salt (halite, starting in 1862) and borates (starting in 1874) to the early 1900s. The central ~2.6 km² of the playa is composed of thick, quite pure halite, and around it on all sides but the west, and under the 15–60 cm thick surface crust (of silt), is massive mirabilite (Fig. 3.42). It is solid, transparent, hard, and up to 4.5 m thick (24 m in one area), while further to the southeast is a zone of massive thenardite (LeConte, in Hanks, 1883). The thenardite occurs in lenses 0.9–1.5 m thick, under 0.6–1.8 m of overburden (silt with some halite), and with mirabilite under it. The total reserves in the deposit have been estimated at >3 million t of Na₂SO₄ (Vanderburg, 1937).

A plant was built to recover sodium sulfate in 1930, first attempting to solution mine or surface leach the mirabilite, recrystallize glauber salt from this brine in ponds in the winter, and then dehydrate it in the ponds during the hot (up to 46°C) summers. This procedure did not prove to be economical, so next the mirabilite was mined, washed, and dehydrated in the plant. Then it was found that the thenardite beds were more extensive than originally anticipated (in a 0.8 km² area), so plant improvements to produce 150 t/day of sodium sulfate from thenardite were made in 1932. In the new operation the overburden was first stripped in a 9–15 m diameter area, trenches dug into the thenardite, and the brine pumped away from the mining area. The thenardite was then blasted and loaded by a gasoline powered shovel (which also had a trench-hoe attachment) into 2 m³ dump cars on a 91-cm industrial track. Rail haulage was necessary because in wet weather or in the winter the slimy mud surface made vehicle travel almost impossible. A small gasoline engine took four to six cars at a time the ~1.6 km to the plant and dumped the ore from an elevated platform into a conveyor feeding a stockpile or jaw crusher. The ~5-cm particles were next repulped in warm recycle brine (to dissolve any mirabilite) and

H₂O. Water for the plant came from two 128–137 m deep artesian wells at the south end of the marsh, with 25–41 cm casings and 200-gpm pumps. Power for the plant was supplied by a 120-HP diesel engine (driving all of the machinery by belts), and a special rail spur was built to the plant by the Southern Pacific Railroad. The plant only operated for 1 year, however, with a maximum production rate of 50 t/day, and during this time suffered both a severe earthquake and a blizzard (Vanderburg, 1937; Tyler, 1935; Rich, 1933).

Wabuska

The Wabuska sodium sulfate deposit is located 1.6 km northeast of the town of Wabuska, in the 48 × 19 km Mason Valley. There are a series of perhaps 20 0.8- to 39 -ha depressions (totaling 100–200 ha) with a 15- to 61-cm-thick, very pure (especially free of other salts) mirabilite–thenardite crust (average >90% Na₂SO₄) throughout the 5–8 km² (several square miles) lowest portion of the valley. There is some overflow drainage during heavy storms from the valley, causing a steady depletion of the deposit. In 1885 there were extensive areas with mirabilite beds 1.8–2.4 m thick, but by 1925 only the crusts remained. Under the crusts are >1.8 m of silt containing up to 22% Na₂SO₄ as mirabilite crystals, and between the crusted basins the low sandy ridges contain 16–40% Na₂SO₄ as thenardite. The mud under the crusts also contains a quite pure sodium sulfate brine to a depth of >2.4 m. It has a density of 1.160 g/cm³ (15–20% Na₂SO₄; Garrett, 1963) and crystallizes thenardite in the summer when the brine reaches a density of 1.262 g/cm³. North of the deposit in the low Tertiary hills the clays and shales contain efflorescent mirabilite to a depth of 5–15 cm. There are extensive lava flows in the adjacent hills, and at least seven low-sulfate geothermal (>66°C) springs along the west side of the valley. The reserves in the surface crusts alone have been estimated at 1 million mt of Na₂SO₄ (Melhase, 1925; Varley, 1924).

Sodium sulfate had been produced from the deposit for several years during 1924–1930 by harvesting the purest crust from the individual depressions. In areas where the crust was not more than 30 cm thick it was broken into slabs by picks and sledges, and when thicker it was broken by explosives. The slabs and lumps were then stacked like cordwood and allowed to dry in the summer (Fig 3.43) for about 2 weeks. At the end of that time it was almost entirely in the thenardite form, and then it was crushed to a –1.28 cm size in a 1 t/hr toothed roll driven by a gasoline engine. After an area had been harvested it was flooded 15–30 cm deep with water from the brine in the underlying mud, from the adjacent hot springs, or from artesian wells produced from a depth of 30–60 m. This dissolved the efflorescent salts and the residue from the previous mining, allowing the area to be reharvested in as little as a few weeks in the summer (primarily as thenardite; Melhase, 1925). The product had a typical analysis of 98.19% Na₂SO₄, 0.23% NaCl, 0.13% Na₂CO₃, 0.23% H₂O, and 0.52% insolubles. It was predicted that if the original crust were leached in place and solar evaporated to produce about 8 cm of crystals, a 99.59% Na₂SO₄ product might be formed (Cole, 1926). More than 1000 t of product was shipped in 1930 (Papke, 1976).

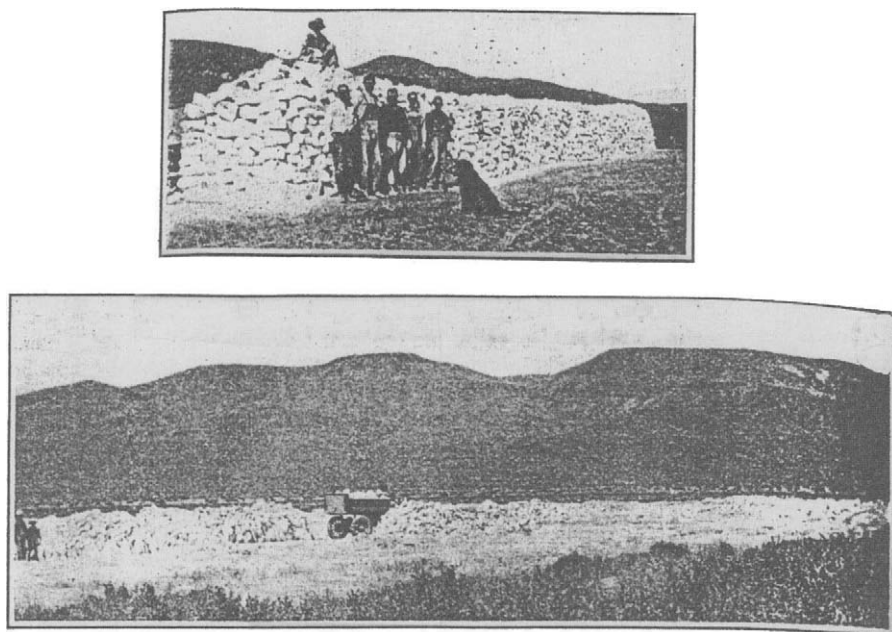


Figure 3.43 The production of sodium sulfate from the Wabuska, Nevada, deposit. *Top*: Slabs of mirabilite stacked to dry. *Bottom*: Playa harvesting procedure. (From Melhase, 1925, by permission of *Engineering & Mining Journal*.)

Other Deposits

Several other sodium sulfate deposits have been reported in Nevada, but have not been produced. In *Diamond Valley* there are a series of small sodium sulfate-crusts as at Wabuska. The valley is located 40–48 km northeast of Eureka and is at an altitude of 1830 m. The individual ponds range from 6 to 490 m in diameter and are in two 2.6-km² groups, ~3 km (several miles) apart. Individual ponds are not connected, but never more than 300 m apart, and contain very pure translucent mirabilite–thenardite crystals resembling bluish-white ice. They are free of iron, nearly free of sodium carbonate and insolubles, and contain less than 0.75% NaCl. The crusts are up to 1.8 m thick (average 1.1 m), and the largest ponds contain about 100,000 t of Na₂SO₄.

The crusts lie on a brine-filled mud base that is very soft and filled with large mirabilite crystals to a depth of 0.9–1.8 m. The sodium sulfate is universally almost twice as thick at the northern ends than at the southern ends, and the soil at the edges of the ponds is ridged up 0.3–2.4 m, again with the ridges on the northern side more than twice as high as those on the southern end. The ridges have steep walls on the inside of the ponds and very gradual tapers on the outside. It is felt that the weight of the mirabilite–thenardite crusts caused them to gradually sink into the

soft sediments, forcing up the ridges. The thicker crusts to the north may have been caused by a general flow of sulfate brine from the north (the predominant valley slope), or possibly from greater solar radiation accumulation from the slightly southern sun position. In the summer days the brine temperature was 1.7–4.4°C higher in the northern ends of the ponds (Blanchard, 1944).

Beds of sodium sulfate have also been reported on the west side of the Smoke Creek Desert at *Buffalo Springs*, east of Buffalo Peak and in the Buena Vista Valley. The playa is 19×6.4 km in size and is encrusted with a heavy efflorescence of sodium sulfate and chloride. A typical analysis is 26.38% Na_2SO_4 , 70.81% NaCl , and 1.94% K_2SO_4 (Wells, 1923). Salt was produced from 3.2 km west of this area from 1875 to 1885 from a 1.133 density brine that was fairly low in sulfate (Papke, 1976). Surface encrustations elsewhere in the *Smoke Creek Desert* have been found to analyze as 27.55% Na_2SO_4 , 18.47% NaCl , and 52.10% Na_2CO_3 . Many springs also contain predominately sodium sulfate, such as *Sou Hot Springs* in the valley east of Buena Vista Valley, *Good Springs* in Clark County, springs on the western border of Smoke Creek Desert and east of Granite Mountains, *Schaffer's* hot spring near Honey Lake, springs north of Granite Mountain, wells in Dixie Valley, and the brine in the high-carbonate Ragtown Soda Lakes (Wells, 1923).

New Mexico

White Sands

There are no important sodium sulfate deposits in New Mexico, but two occurrences have been either briefly operated or examined for potential production. The White Sands deposit occurs in Dona Ana County, 40 km west of Valmont (which is 16 km south of Alamogordo and 130 km north of El Paso) in a playa between the San Andres Mountains and the White Sand Dunes. The floor of the basin is composed of gypsum, and in the lowest or south-central part the top 0.3–1.3 m of gypsum is mixed with thenardite (surprisingly, no glauberite was reported). The structure from near the surface to some depth is also filled with a nearly saturated, fairly pure sodium sulfate brine. Two successive companies did experimental processing studies for a few years starting in 1919, but no production was ever recorded (Wells, 1923).

Carlsbad Brine

A series of shallow water wells in Dona Ana County, west of the Pecos River and near the Carlsbad potash mines, were drilled between 1906 and 1934 and found to be nearly saturated with sodium sulfate. The brine was at a depth of 49–52 m in the hydrating anhydrite (being converted to gypsum) of the Castile Formation. More than 30 test wells located at least three areas with potentially economic brines. Their average analyses was 18.7% SO_4 , 2.2% Cl , 0.2% CO_3/HCO_3 , 0.5% B_4O_7 , 3.8% Na , 3.5% Mg , 0.5% K , 29.2% total solids, and a density of 1.302 (equivalent to 11.6% Na_2SO_4 and 12.9% MgSO_4 ; Lang, 1941). These wells were produced from 1951 to

1957 and trucked to a processing plant at Monahans, Texas, but the formation depleted rapidly and had to be abandoned (Weisman and Tandy, 1975). Astrakanite ($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$), loeweite ($2\text{Na}_2\text{SO}_4 \cdot 2\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$), and vanthoffite ($3\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4$), have all been found in small quantities in the Permian Salado Formation marine evaporites (Madsen, 1966).

North Dakota

The zone of sodium sulfate lakes in Canada extends slightly into Montana, and much more into North Dakota where there are literally hundreds of saline lakes (Fig. 3.44), a few of which have been considered as potential sodium sulfate deposits. Five of the lakes were extensively drilled and sampled, and three others were examined in less detail by Lavine (1935). There has also been scattered drilling and sampling of these and other lakes since that time (see Murphy, 1996, and Binyon, 1952). The lakes are very similar to the ones in Canada, occurring in the most arid part of the state, being deposited within the past 12,000 years (since the last glaciers retreated), only occurring in glacial moraines consisting of coarse sand and gravel till, and most of them lie in old glacial-filled (30–90 m thick) valleys or river beds (with the glacial sediments now often containing aquifers). Also, the generally steep sides (below the ground level) of the thick deposits implies that they may have formed from the melting of buried blocks of glacial ice, forming deep sinkholes that could collect drainage from the surrounding area. This allowed sodium sulfate deposits to accumulate as is now occurring in the deep Canadian Freefight and Deadmoose Lakes.

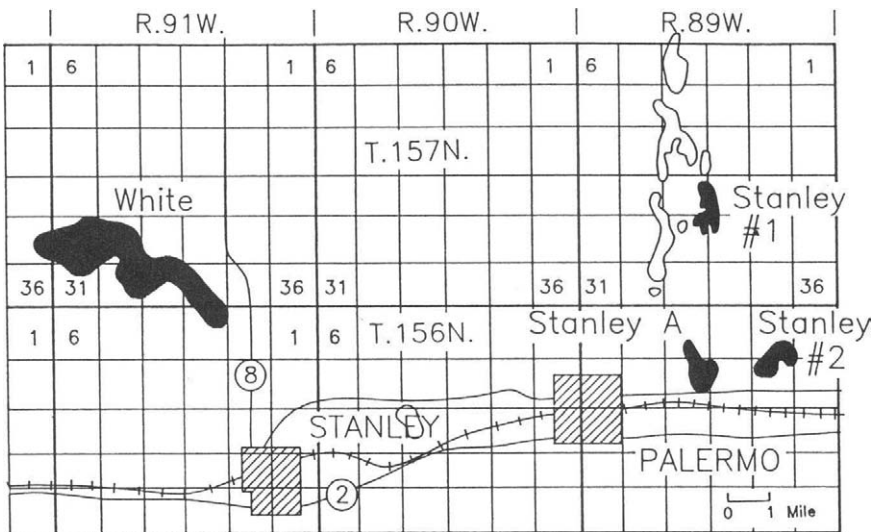


Figure 3.44 Typical occurrence of the North Dakota sodium sulfate lakes. (From Murphy, 1996, by permission of the North Dakota Geological Survey.)

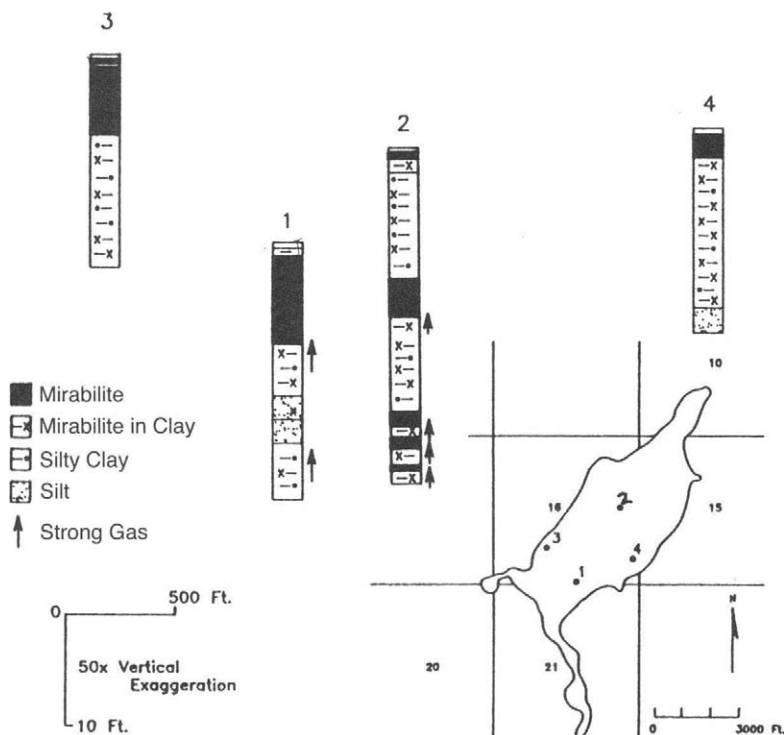


Figure 3.45 Map and stratigraphy of Grenora No. 1 Lake, North Dakota. (From Murphy, 1996, by permission of the North Dakota Geological Survey.)

The difference between the lakes containing sodium sulfate deposits and those with more dilute waters appears to be that the former are in more completely closed basins, have more impervious bottoms, are lower lying, and have springs and sometimes other lakes draining into them. This has allowed drainage waters from the mineral-laden soil (often containing both gypsum and pyrites) to accumulate, evaporate, and eventually somewhat selectively crystallize mirabilite in the autumn and winter. Many of the lakes become completely dry in the late summer, and later re-flood, dissolving some or all of the crystals in the late spring. The sodium sulfate deposits in North Dakota contain from 5 cm to 24 m of mirabilite, but only average ~1 m of potential ore. Grenora 1 (Fig. 3.45) is somewhat larger, averaging 1.6 m in thickness (Murphy, 1996; Slezak and Last, 1985; Lavine, 1935).

Chemical Analyses

The chemical analyses of the deposits in North Dakota are similar to those in Canada, with some having a high sodium carbonate content. Lavine (1935; Table 3.22) analyzed and averaged large numbers of samples from five lakes, but as with

Table 3.22
Analyses of Various North Dakota Sodium Sulfate Deposits (wt%)^a (Levine *et al.*, 1935)

	Na ₂ SO ₄	MgSO ₄	CaSO ₄	NaCl	Na ₂ CO ₃	NaHCO ₃	Insol.	No. of samples
Brush, SE Dep. ^b	77.8	2.5	0.3	0.7	2.3	0.5 ^c	15.9	—
Douglas, crust ^b	78.9	6.7	0.5	0.3	0.2	0.7 ^c	12.7	—
Grenora 1 ^d	89.79	1.24	1.50	1.64	—	0.78	5.05	61
Springs ^d	17.47	7.07	0.27 ^f	2.22	0.10	—	107 ^g	19
Wells ^{d,e}	4103	1650	1057	208	83	887	215 ^h	3
Crust ^d	94.09	3.25	0.49	0.78	—	0.86	0.53	—
Grenora 2 ^d	82.71	1.81	1.43	1.14	—	0.88	12.03	128
McKone ⁱ	84.60	1.09	1.71	1.09	0.87 ^g	0.64	10.00	18
Miller ^d	90.85	2.82	1.22	0.87	0.05	0.60	3.59	83
North	84.92	3.68	0.36	0.51	0.14	0.39	10.00	—
StadyE ^b , crust	71.0	9.2	0.2	4.0	—	1.3 ^c	14.3	—
Deposit	73.4	6.3	0.3	0.7	0.1	0.3 ^c	18.9	—
Stanley 1 ^d , Dep.	74.78	1.13	0.50	0.48	6.27	3.48	13.36	45
Deposit ^b	59.5	4.4	0.2	—	11.2	1.1	23.6	—
Crust ^b	59.2	3.3	0.2	—	3.4	0.8	33.1	—
Stanley 2 ^d	83.32	1.05	0.57	0.41	2.94	2.95	8.76	56
Stink ^b , Crust	79.6	13.5	1.6	1.0	—	0.4 ^c	3.9	—
Deposit	64.0	13.8	1.8	1.3	—	0.6 ^c	18.5	—
Westby	86.28	0.65	1.75	0.85	—	0.47	10.00	—
Crust ^b	83.1	2.7	1.0	0.4	—	0.5 ^c	12.3	—
White ^b , Crust	83.9	9.1	0.6	0.1	0.2	0.6 ^c	5.5	—
Average values:								
Crust ^b	76.4	7.4	0.8	0.4	0.8	0.4 ^c	13.8	6

(continues)

Table 3.22
(continued)

	Na ₂ SO ₄	MgSO ₄	CaSO ₄	NaCl	Na ₂ CO ₃	NaHCO ₃	Insol.	No. of samples
Average of the Deposits:								
High CO ₃ /HCO ₃ ^d	79.05	1.09	0.53	0.45	4.60	3.22	11.06	2
High CO ₃ /HCO ₃ ^b	71.1	0.5	0.2	0.3	7.1	0.7 ^c	20.1	2
High MgSO ₄ ^b	68.8	10.2	1.1	1.0	0.1	0.1 ^c	18.7	2
Others ^d	87.78	1.96	1.38	1.22	—	0.77	6.89	3
Others+mud ^b	19.3	2.9	0.4	1.2	1.4	0.3	74.5	10

^aAll samples on an anhydrous basis, and corrected to 100%. Some with an assumed 10% insolubles content (they were listed on an insolubles-free basis).

^bBinyon (1952). Corrected to 100% on an anhydrous basis (all samples were reported with a high-to-very high water and insolubles content).

^cIncludes KHCO₃.

^dLavine *et al.* (1935).

^eppm.

^fCa(HCO₃)₂.

^gAl₂O₃ (ppm).

^hFe₂O₃ (ppm).

ⁱSchultz and Lavine (1942).

Cole (1926) in Canada reported the data as compounds, some of which were impossible to be present together. Binyon (1952) unfortunately reported all of his analyses with a great deal of mud (19–90% insolubles) and ice (30–67% water). Grossman (1949; Table 3.23) only analyzed brine, and many of his lakes were quite dilute, perhaps indicating an early spring sampling before all of the surface crust was dissolved, giving a disproportionately low sodium sulfate and high magnesium content. However, even with these uncertainties, the analytical data are quite useful.

The brine data of Grossman (1949) indicate that many of the lakes, as in Alberta, have a high carbonate/bicarbonate content (6 out of his 13), and only a few are high in magnesium (2 out of 13). This agrees with Lavine *et al.*'s (1935) analyses of the deposits, where 2 out of their 7 had a high- CO_3/HCO_3 content, and none were high in Mg. However, Binyon's (1952) mirabilite analyses indicated only 2 out of 14 with high- CO_3/HCO_3 , but all 14 deposits and the 6 crusts that were analyzed had considerable Mg (Which of course is impossible for the 2 deposits with high- CO_3/HCO_3). This makes it hard to characterize the deposits, but it appears that they are basically similar to those in Alberta. Grossman (1949) reported that many of the lakes contained prolific brine shrimp (*Artemia salina*), and the salt-tolerant plant *Salicornia rubra* grows at their edges. Each of the drilling programs found considerable gas in the organic-rich sediments directly under the mirabilite beds (presumably CO_2 and H_2S), with the latter occasionally strong enough to stop the drilling for safety reasons.

A list of the 14 largest lakes is given in Table 3.24, with rough estimates of their sodium sulfate content. The total tonnage of Na_2SO_4 in all of the lakes is estimated to be 19 million t, but it is seen that about one-third of this is claimed as a low-percentage mixture in mud and is probably not recoverable. Some of the other deposits are either deeply buried or occur as thin beds interlayered with thick mud beds that would also be hard to recover, making the reserves estimates appear to be optimistic compared to the corresponding Canadian estimates. However, most of the deposits should be as easy to mine as the many that have been operated in Canada, since they are very similar in structure. Descriptions of a few of the lakes follow.

Miller Lake

The largest deposit is *Miller Lake*, with an area of 263 ha (650 ac; Fig. 3.46) and reserves of 5.7 million of Na_2SO_4 . It occurs in a collapsed depression of glacial till and lake bed sediments, and east of it are a series of glacial thrust ridges. It normally contains 0.3–1 m of brine, although it occasionally totally dries up. In one 36 ha (90 ac) area the mirabilite beds are comparatively clean, up to 15 m thick, and contain 2.2 million t of Na_2SO_4 . However, even though the cumulative average thickness of the mirabilite beds throughout the lake was 3.3 m, many of the individual beds (especially at depth) were only 0.1–1 m thick and interlayered with clay. As with each of the other sodium sulfate lakes, the clay had a high organic content, there was considerable gas under the mirabilite, and the brine shrimp were prolific in the lake's waters. This lake has been extensively examined for commercial sodium

Table 3.23
Brine Analyses for Various North Dakota Sodium Sulfate Lakes (wt%) (Grossman, 1949)

	Na	Mg ^a	Ca ^a	SO ₄	Cl ^a	CO ₃ ^a	HCO ₃ ^a	SiO ₂ ^a	Fe, Al ^a	TDS
Carpenter ^c	1.08	300	100	1.99	600	600	2900	—	—	3.52
Crooked ^a	652	2037	20	8380	613	180	—	—	—	13970
Douglas A	1.29	1100	42	3.03	212	672	—	—	—	5.19
Douglas A ^c	1.48	1800	100	3.22	1700	600	2400	—	—	5.36
Genora 1 ^{g,h}	2.87	21,500	744	13.70	10,500	—	2000	8	—	20.25
Genora 2 ^{g,i}	2.40	4540	285	8.05	6710	219	1000	17	1.5	11.82
Horseshoe	1.52	12	28	2.56	429	2600	1760	31	21	4.49
Horseshoe ^{g,j}	3.64	52	27	4.03	4170	15,500	34,100	203	3.1	11.33
Lower Lostwood	1.75	1020	14	3.60	702	3010	—	—	—	9.32
McKone	4.67	13	13	8.25	3900	4650	2290	68	32	14.26
Miller ^{g,k}	2.43	8040	191	10.79	5350	435	1840	3	—	14.91
Stanley A										
Spring ^a	354	9	16	636	8	106	—	48	13	1960
Brine	4.99	199	20	8.06	58	12,000	16700	1340	139	19.98
Brine ^c	2.20	900	100	2.79	400	13,200	400	—	—	6.49
Stink	2.38	2980	915	6.20	1300	144	—	—	—	12.03
Unnamed	1.36	11	7	2.62	928	235	98 ^b	70	130	4.42
Westby A	4.67	6020	1720	12.43	947	196	366	334	217	19.25
Westby B	4.26	29	12	8.15	2320	9600	3850	1380	168	15.71
Westby C	1.69	6	219	3.04	3840	278	1960	25	200	12.81

White	2.85	125	58	5.87	268	840	—	—	—	9.43
Cottonwood ^{a,f}	2400	20	24	2640	532	1000	1090	90	18	8530
White ^c	1.61	1300	100	3.56	500	900	2300	—	—	5.68
White ^{g,i}	2.08	156	75	7.92	527	636	2360	103	17	10.26
Groundwater:										
In bedrock ^{a,d}	687	19	50	643	85	—	1110	13	0.14	2061
In till ^{a,e}	185	129	205	384	136	—	643	26	0.03	1828
Average values, (Number of lakes):										
High CO ₃ /HCO ₃ (3)	3.48	203	33	5.63	1950	10,420	10,100	722	83	12.29
High Mg (3)	3.32	11,850	885	10.42	5600	210	1400	115	72	18.14
Others (9)	2.10	1210	189	4.74	2150	1170	1210	27	41	9.10

^appm.^bOH, not HCO₃.^cBinyon (1952).^dAlso B 0.55 ppm, K 10, F 1.2, NO₃ 2.4, pH 8.6, 49°F.^eAlso B 0.40 ppm, K 11, F 0.47, NO₃ 422, pH 8.1, 49°F.^fFlows into White Lake.^gMurphy (1996) corrected for assumed densities.^hAlso, ρ 1.19, K 3510 ppm, F 0.7.ⁱAlso ρ 1.108, K 1040, F 0.5.^jAlso ρ 1.103, K 341, F 6.3.^kAlso ρ 1.14, K 1700, F 0.6.^lAlso ρ 1.09, K 230, pH 9.10.

Table 3.24
Size and Estimated Mirabilite Reserves of the Larger North Dakota Sodium Sulfate Lakes (Murphy, 1996)

	Brine			Crust		Beds		Mud		Total ^c
	Area ^a	Th ^b	Ton ^c	Th ^b	Ton ^c	Th ^b	Ton ^c	Th ^b	Ton ^c	
Miller	600	1.0	0.074	0.6	0.5	11.8	7.6	15.4	4.8	13.0
Grenora 1	500	—	—	0.28	0.2	5.18	2.8	16.0	4.1	7.1
Grenora 2	644	1.5	0.114	—	—	3–16.1	5.01	2–11	1.17	6.38
White	2647	1.16	0.39	0.88	2.36	—	—	2.51	1.86	4.6
Westby B	386	—	—	1.16	0.14	9.08	3.7	—	—	3.8
Stink	153	—	—	0.39	0.014	10.46	2.1	0.52	0.056	2.2
Stanley A	316	0.1	0.0035	0.14	0.0395	3.6	1.3	3.56	0.774	2.1
Stady E	132	—	—	0.10	0.0027	9.66	1.77	2.03	0.071	1.8
North	284	—	—	0.30	0.12	2.06	0.32	11.6	1.326	1.8
Stanley 1	124	—	—	5.0	0.66	—	—	2.0	0.13	1.0 ^d
Westby A	118	—	—	0.15	0.024	3.0	0.38	8.1	0.5	0.9
Stanley 2	230	1.5	0.04	—	—	2.5	0.62	1.0	0.12	0.78
McCone	223	—	—	0.14	0.042	2.25	0.537	1.5	0.175	0.75
Westby C	57	—	—	3.85	0.12	9.8	0.54	—	—	0.66
Total ^d	—	—	0.6215	—	3.9882	—	26.679	—	15.082	46.369

^a Acres.

^b Formation thickness, ft.

^c Reserves, millions of short tons of mirabilite. Total 18.6 million mt Na₂SO₄.

^d Lavine (1935). Also Rice Lake, 2.2 million t mirabilite.

^e The total tonnage listed by Schultz and Lavine (1942) was: Grenora 2, 11; Miller, 5; McKone, 3; Grenora 1, 1.75; Stanley 1 and North, 1; Stanley 2, 0.6; Hansen (1964) estimated: Grenora 2 5.5, White 4.6, Miller 2.8, Stanley A 2.1, Stady E 1.8, McKone 1.5, Stink 1.2, Grenora 1 1.0, Westby A 0.9 and Stanley 1+2 0.9; total 23.7.

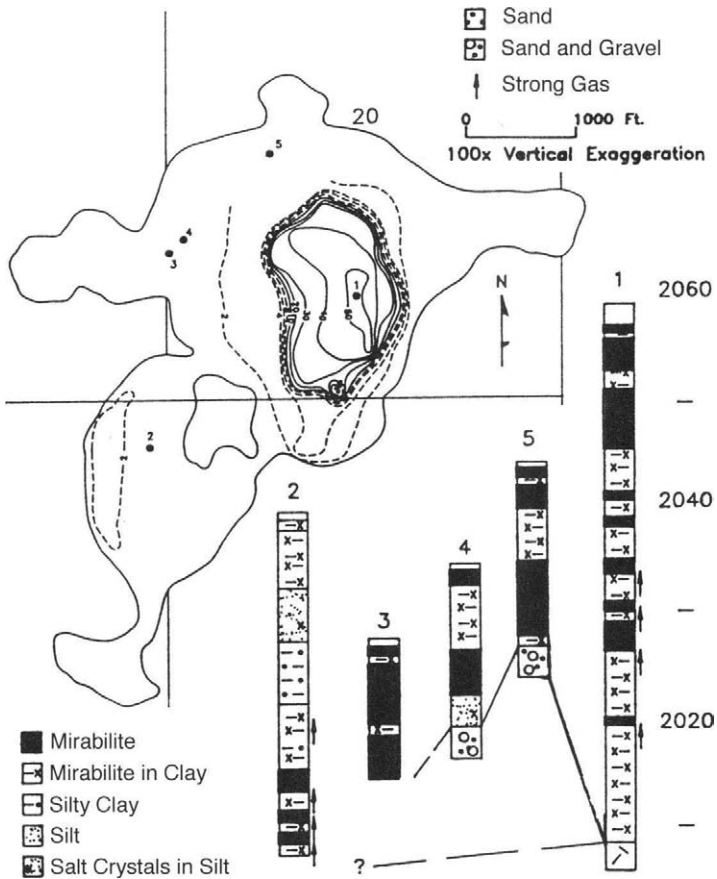


Figure 3.46 Map and stratigraphy of Miller Lake, North Dakota. (From Murphy, 1996, by permission of the North Dakota Geological Survey.)

sulfate production, including one semicommercial, large pilot plant operation, and one announcement of actual production that was later canceled (Garrett, 1964).

Grenora Lakes

The Grenora area contains three medium-sized sodium sulfate deposits, Grenora 1, Grenora 2, and Stink (Fig. 3-45), with combined reserves of 6.9 million tons of Na_2SO_4 . They are located in the glacially buried Missouri River channel that contains 120–150 m of glacial till filled with the Grenora Aquifer. The lakes flood with 0.1–1 m of brine in the spring, and generally dry up in the summer. In the 200-ha Grenora 1 the mirabilite beds average 0.76 m in thickness, with a maximum thickness of 9.1 m. Grenora 2 contains one deep 36-ha zone of mirabilite that contains

about 15 m of mirabilite (interlayered with in excess of 21 m of insoluble lacustrine sediments). However, the average thickness of mirabilite for the entire lake is 3.6 m. Stink Lake has not been drilled extensively, or deeper than 3.6 m (except one hole at 5 m), but at least an upper 2.4- to 3-m thick mirabilite bed with a lower 1.2-m bed is indicated (Murphy, 1996).

Several other articles have been written on the North Dakota sodium sulfate deposits, including those by Komor (bottom sediments; 1994), Grossman (origin; 1968), Hansen (general; 1964), Witkind (general; 1952), Schultz and Lavine (general; 1942), Lavine and Feinstein (general; 1936), and Anon. (general; 1934).

Oregon and Washington

The majority of the sodium sulfate lakes in Oregon and Washington are similar to those in southwestern Canada. Their basins were also formed by glacial action in mountainous terrain during the same period, and their minerals were also leached largely from the resulting glacial till. Their lakes are also fairly small, and there is a diversity of minerals (Table 3.25).

In Oregon and Washington there are about an equal number of predominately sodium sulfate, sodium carbonate, or magnesium sulfate lakes, and the majority of the lakes contain major amounts of all three salts. The same phenomena of most of their water entering from springs or aquifers and the somewhat selective crystallization of the high-hydrate salts (thus allowing a greater seepage loss of sodium and potassium chloride, etc.) occurred. The rock types that were scoured, crushed, and carried by the glaciers were also varied, and often differed widely over short distances. This allowed lakes in very close proximity to frequently have quite different brine chemistries.

The majority of lakes with a permanent mirabilite deposit or a larger amount of sodium sulfate in their brine are in the Okanogan Plateau in the north-central area. The climate is semiarid, the winters cold, and the intermittent lakes usually flood with 0.3–0.6 m of water in the spring and become dry in the summer. There are 11 lakes with bedded sodium sulfate deposits of modest tonnage (*BJ, Cameron, Huan, Lawson, Morris, Murray, Penly, Stevens, Tribal, Virginia*, and 32), and three of these are perennial lakes. Some of them have the appearance of “spotted lakes,” where the lake bed consists of many small round-to-ovoid zones (often 3–6 m in diameter) of pure salts surrounded and separated by low mud ridges. It is thought that these crystal zones formed by the flow of groundwater up to the surface (where it evaporates and deposits salts) in many small, fairly uniformly spaced veins, rather than in larger springs. Each of the lakes with bedded deposits has zones of pure massive mirabilite (it averages 3.2% sodium carbonate and very little insolubles; there are some layers of thenardite in the lakes with a high NaCl content) with some mud, and mirabilite crystals in the mud. On average, the lakes are 5.4 ha (13.3 ac) in size, they contain 0.4-m thick pure mirabilite beds (with zones up to 2.2 m thick), and their equivalent Na_2SO_4 content is 27,000 t. The sum of the Na_2SO_4 in all

Table 3.25
Analyses of Some of the Oregon–Washington Sodium Sulfate Lakes (wt%) (Bennett, 1962)

	Na ₂ SO ₄	MgSO ₄	NaCl	Na ₂ CO ₃ /NaHCO ₃	Insol.	TDS	Density	1000 t Na ₂ SO ₄
No. 13, brine	14.25	11.74	2.55	0.24	—	28.78	1.304	17
Salts	88.4	1.2	0.1	—	10.3	—	—	—
No. 16, brine	0.96	0.01	0.23	0.81	—	2.01	1.014	—
No. 32, brine	3.90	0.01	0.25	0.32	—	4.48	1.037	12 ^a
Crust	99.18	0.18	0.23	0.33	0.08	—	—	—
BJ, brine	6.63	—	0.25	0.17	—	7.05	1.060	23 ^a
Salts	90.5	0.2	0.6	0.6	8.1	—	—	—
Cameron, brine	12.01	0.10	0.64	0.27	—	13.02	1.118	24 ^a
Cook, brine	4.22	1.39	0.18	0.09	—	5.88	1.050	4
Huan, brine	11.67	0.48	0.94	0.01	—	13.10	1.119	75 ^a
Salts	87.2	0.5	0.6	0.6	11.1	—	—	—
Lawson, brine	4.75	0.19	0.18	0.06	—	5.18	1.043	63 ^a
Morris, brine	4.45	0.14	0.16	0.08	—	4.83	1.040	9 ^a
Murray, brine	11.81	1.05	0.17	0.10	—	13.13	1.123	18 ^a
Patterson, brine	0.90	0.81	0.05	0.04	—	1.80	1.013	0.3
Crust	39.8	51.9	0.4	1.3	6.6	—	—	—
Penley, brine	16.88	0.73	0.70	0.06	—	18.37	1.171	31 ^a
Soap, brine	3.59	0.02	0.35	1.12	—	5.08	1.041	330 ^a
Stevens, brine	4.08	—	0.18	1.24	—	5.50	1.047	10 ^a
Sulfate, salts	76.7	0.1	1.1	1.4	20.7	—	—	—
Then. ^b crust	96.3	—	1.3	1.2	1.2	—	—	—
Virginia, brine	12.98	0.08	0.35	0.01	—	13.42	1.121	6 ^a
Salts	70.2	1.0	0.4	—	28.4	—	—	—
Average brine analyses (number of lakes):								
High-Mg (4)	7.80	3.75	0.74	0.12	—	12.41	1.123	—
High-CO ₃ (3)	2.88	0.01	0.25	1.06	—	4.20	1.034	—
Others (8)	9.16	0.22	0.43	0.12	—	9.93	1.089	—

^aRivisto (1963).

^bThenardite.

11 lakes and all three of their zones is only 296,000 t. Four other lakes (*Cook*, *Farley*, *Omak*, and *Soap*) in this area contain larger amounts of sodium sulfate, but as a very dilute or mixed-salt brine (Rivisto, 1963).

A number of other lakes have also been reported with a lesser amount of sodium sulfate in their brine or mirabilite beds. Among these Bennett (1962) listed several others in Washington's Okanogan Plateau: *Bitter*, *Poison*, *Sulfate* (now flooded), and *Wannacut* (the last has brine only). In southern Oregon there are many lakes of the more normal desert type, but almost none have a preponderance of sodium sulfate or bedded mirabilite. Many are high-carbonate lakes, and all have a fairly equal mixture of salts. However, some do have a fairly large amount of sodium sulfate in their brine (Garrett, 1992).

Commercial Production

A number of attempts have been made to commercially produce sodium sulfate from the Oregon–Washington lakes. At *Sulfate Lake* (Fig. 3.47) in 1916–1917, 2500 t of product was shipped to a paper mill in Minnesota, which was claimed to be the first natural U.S. salt cake used in the manufacture of kraft paper (although Soda Lake in California may actually have been the first). A fairly pure bed of thenardite with some mirabilite from the northeast side of the lake was harvested in the summer and spread thinly over a platform to dry and dehydrate. The powdery product was then loaded and shipped in bulk to the mill. During the early 1930s some mirabilite was also harvested from the 1.3-m thick mirabilite beds in seven 21–30 m diameter “spots” in the center of *Virginia Lake*, and a loading ramp and platform still remain. A similar operation was conducted on *Lake 32* and *Morris Lake* by scraping thenardite from the surface and piling it on the shore. The scraping was done by a homemade dragline on Morris Lake, and several buildings were constructed on the south and east sides of Lake 32 to support their operation. During 1942–1943 a >\$100,000 refinery was built at Monse to produce 100 t/day of sodium sulfate from *Lawson Lake*. The plant had three 300-HP boilers, three centrifuges, a rotary dryer, melting and settling tanks, an evaporator, pumps, and conveyors. A road was constructed from the lake to the town, and the brine was pumped from the lake to a small nearby lake in preparation for harvesting the mirabilite. However, apparently no production was ever obtained. Some experimental work was also done on *Cameron*, *Hauan*, *Murray*, and *Penley lakes* (Bennett, 1962).

Texas

Fairly shallow brines containing a high concentration of sodium sulfate occur in the northwest corner, High Plains region of Texas. They are in a different formation, but somewhat similar to the nearby southeastern New Mexico brines trapped in the generally more limited near-surface aquifers of the porous gypsum in the Castile Formation of the Delaware Basin (Lang, 1941). Most of the Texas occurrences are in the Ogallala Formation which has formed the area's surface “plains,” and slopes

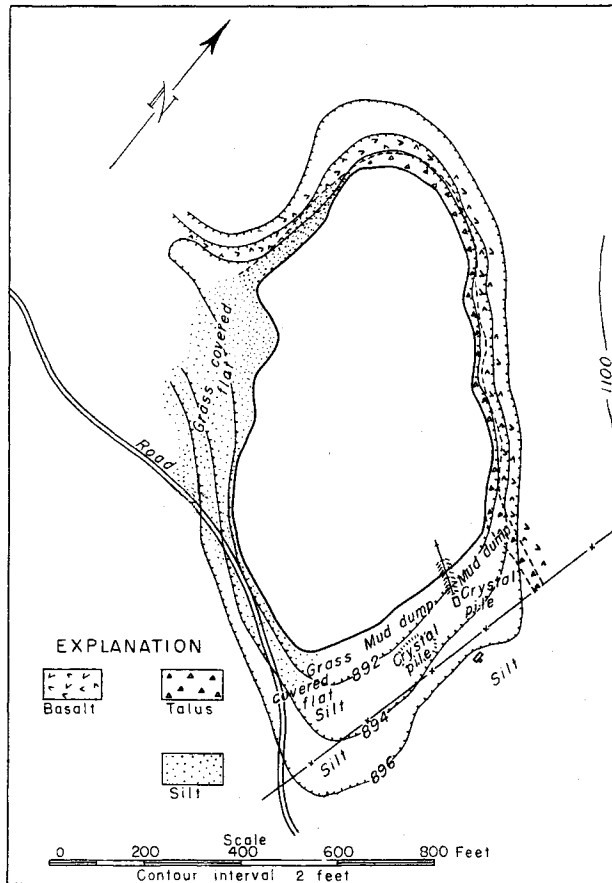


Figure 3.47 Sulfate Lake, Washington. (From Bennett, 1962, by permission of the Washington State Geology and Earth Resources Division, Department of Natural Resources.)

at a rate of 0.9–1.1 m/km (5–6 ft/mi). It also generally occupies former ice age river channels that extend on the west side of the Rocky Mountains from North Dakota to Texas. As these channels began to be filled about 40,000 years ago, many broad closed basins were formed from tectonic movement, sand drifts, or other closure mechanisms. Much of the fill material was detritus resulting from erosion of the reemerged Rocky Mountains 2–5 Myrbp (during the Pliocene) and carried to Texas by streams or sheet floods, causing much of the fill to be somewhat porous. The groundwater that flowed into these basins during the filling period had an elevated sodium sulfate content, and during interglacial high-evaporation periods the sodium sulfate was concentrated and occasionally formed beds of mirabilite. As the ice age was concluded about 12,000 years ago many playas had been formed, but

because of the dilute sodium sulfate content of the water that periodically flooded their surfaces, most of the sodium sulfate was in the subsurface aquifers or as buried beds of mirabilite.

At least 13 such deposits have been noted, and four of them in Caines, Lynn, Terry, and Ward counties have been worked commercially to recover sodium sulfate. Other counties with brine deposits include Andrews, Bailey, Cochran, Crane, Hockley, Howard, Lamb, and Midland. Some of the brines are moderately weak, such as at Silver Lake (Cochran County, 7.5% Na_2SO_4), and Double Lake (Lynn County), Coyote and Yellow Lakes (Hockley County) and Illusion Lake (Lamb County) with 2–3% Na_2SO_4 brines. Elsewhere in the much deeper Permian Formation sodium sulfate brines also occur, but because of their depth they have not been commercially exploited (McIlveen, 1999; Anon., 1960; Sellards and Evans, 1960).

Soda Lake

The first deposit operated was the 65-ha (160 ac) Soda Lake 21 km south of Monahans in Ward County, producing more than 1 million t of sodium sulfate from 1933 to 1970. It operated on brine rich in sodium sulfate and sodium chloride, with lesser amounts of magnesium and potassium salts, and pumped from an aquifer 30.5 m deep. There was an upper bed of mirabilite 0.9–1.8 m thick at a depth of 0.3–0.9 m, and a second thin bed separated by 9 m of red clay. The deposit had been explored by drilling, several processing methods were tested, and the initial plant constructed at a cost of \$350,000 by the Ozark-Mahoning Company (Tyler, 1935; Wells, 1923). In a later article Weisman and Anderson (1953) noted that they pumped brine from two aquifers. At a depth of 18 m a weak brine with a density of 1.16 and 7–8% Na_2SO_4 was pumped into solar ponds on the lake's surface in the summer to be concentrated to a density of 1.18, or 10% Na_2SO_4 . This strong brine was then pumped to the plant to join or replace a stronger brine pumped from a 27-m depth. It had a density of 1.18–1.20 and 11.2% Na_2SO_4 (8.2% SO_4 , 6% Cl and 1.8% Mg), but could only be pumped at a rate of 3–18 gal/min/well without serious dilution. This required a large well field, and the brine supply was more limited than the shallower, weaker brine. Other articles on this operation have been presented by Anon. (1953) and Anon. (1932).

Cedar Lake

The 21 km² (~5000 ac) Cedar Lake playa is near Seagraves, Texas, and contains a strong sodium sulfate brine from near the surface to a 30.5-m depth, as well as a moderate amount of mirabilite in the aquifer zone. The richest brine is at a depth of 12–30.5 m and in 1999 contained ~10% Na_2SO_4 , 12.5% NaCl, ~1% Mg, lesser amounts of K, 100–140 ppm Br, and very little organics or hydrogen sulfide. In 1994 the analysis was listed as 10.5% Na_2SO_4 and 14% NaCl, whereas in 1979 it was reported to contain 10.6% Na_2SO_4 , 10.6% NaCl, 3% MgCl_2 , and some other salts. A slightly weaker brine (8% Na_2SO_4) lies above the deeper brine and in the lake margins. The lake is at an elevation of 920 m (3020 ft) in a natural depression 15–21 m below the surrounding plateau, and its sediments are >25 m thick. In addition to containing brine, mirabilite, alluvial gravel, and silt they also contain clay, black mud

with some H_2S , and blue-green algae. The lake receives a small amount of surface drainage that rapidly evaporates and then seeps into the underlying sediments, as well as a subterranean flow of brine that in places (springs) is said to contain up to 10% salts with a high sodium sulfate content. There also appears to be some capillary evaporation in the summer that continues to increase the concentration of the underlying brine (Frei, 1999; McIlveen, 1999; McIlveen and Cheek, 1994; Bhan, 1979).

Brownfield Lake

The Brownfield (or Lost Draw) *Lake* deposit is located 16 km east of Brownfield, with a brine-containing area of 4 km^2 that lies partly outside the boundary of the present somewhat indistinct playa surface. At a depth of 9–30.5 m there are beds of mirabilite 1–4 m thick, interbedded with thin layers of clay and silt. A saturated brine was produced by solution mining this zone that analyzed 15% Na_2SO_4 , 10% NaCl , and much less Mg and K (Weisman and McIlveen, 1983; a quite different analysis was given by Bhan, 1979, as 13.5% Na_2SO_4 , 3% NaCl , 6.8% MgCl_2 , and some other salts). Because of its high H_2S and organics content the brine had to be aerated and filtered before it could be used (McIlveen, 1999). *Rich Lake* is 19 km north of Brownfield Lake and produced sodium sulfate from a mirabilite bed averaging 2 m in thickness. The brine was shipped by pipeline to the Brownfield plant. *Mound Lake* is 13 km north of Brownfield Lake, and starting in 1981 also shipped its brine there. It has an area of 5 km^2 and considerable mirabilite, and the brine (similar to that at Cedar Lake) occurs to a depth of 24 m (Weisman and McIlveen, 1983). As of 1999 the 64,000 mt/yr Brownfield operation was maintained in a standby mode, and the Cedar Lake plant at Seagraves was the only Texas deposit in production (Anon., 1998).

Utah

The Great Salt Lake

There are several playas in Utah, as with the other western states where mirabilite has been reported, but by far the largest occurrence is in the Great Salt Lake. There it is found in three types of deposits: (1) During arid periods mirabilite crystallizes from the lake brine in the winter, depositing throughout the lake, and much of it floats (mirabilite's density is 1.5; the brine is 1.22–1.25), forming large wind-blown banks on the shores (particularly in the southeast corner). (2) There are also buried deposits in this corner and west of Promontory Point (in the north center of the lake). (3) Finally, there is considerable sulfate in the brine. The total of these sources is 408 million mt of Na_2SO_4 (Eardley, 1966).

Shoreline Deposits

In December mirabilite begins to precipitate during arid periods (after the brine has become quite concentrated in the summer), and the brine temperatures may drop to -4°C . Large banks 0.9–1.2 m thick, rising 0.3–0.5 m above the water and extending 60 m or more in width, can be built by the waves for many miles in the shallow shore areas. Rafts of mirabilite have been reported some distance from the

shore, and the entire bed of the lake becomes coated with mirabilite. The deposits eventually become quite solid, although not very hard, resembling a dense snowbank. As winter and spring water floods the lake, and the brine warms, most of the mirabilite quickly dissolves (Adams, 1938).

In the south and southeast edges of the lake there are buried deposits of mirabilite, often under ~ 0.6 m (5 cm–1.2 m) of calcareous sand (rounded chemical precipitates from the lake). The beach has a very gentle slope of a few centimeters to 0.3 m per 30 m, allowing a band of mirabilite to have formed 305–610 m wide and 0.3–1.8 m thick. It is quite free from other soluble salts, containing less than 2% NaCl (primarily from occluded brine), but it is mixed with about 50% of the calcareous sand. It forms a very hard, dense, brittle mass, and holes through it (as for pilings for structures) have usually been made with steam lances, which cut through very easily. It rests on soft silt or clay that is quite different from the sand above it, and there are numerous small sinkholes that have developed from fresh-water entry into the beds. It is not known whether it formed from the winter deposit being covered (or codeposited) with sand, or from the subsurface crystallization of a high-sulfate brine in the winter (Adams, 1938; Wilson and Wideman, 1957).

Promontory Point

A second occurrence of mirabilite was discovered when the Southern Pacific Railroad Co. built a causeway across a narrow portion of the lake in its north-central area (from Promontory Point to Lakeside in 1900–1903). As they drilled the lake to determine the strength of the sediments, they encountered a mirabilite bed 4.6–9.8 m thick, 4.6–7.6 m below the bottom of the lake, extending from the shore to 15 km into the lake (to about its midpoint; Fig. 3.48). It is interbedded with clay

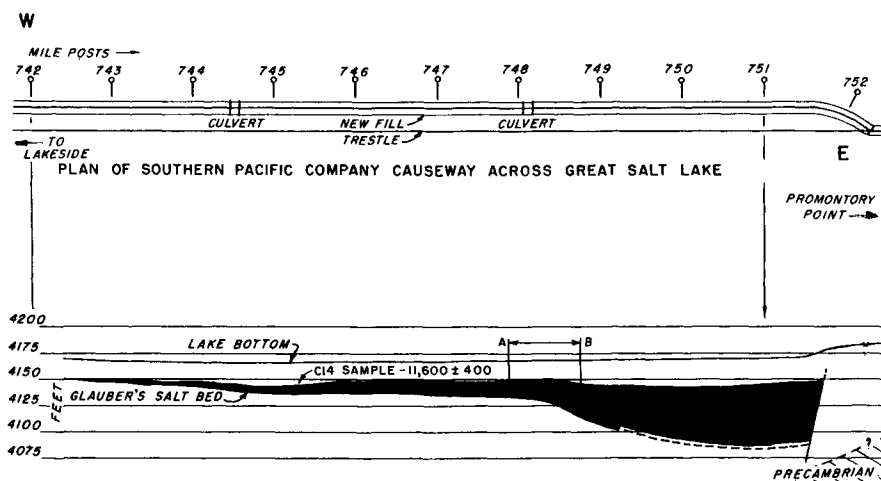


Figure 3.48 The mirabilite bed under the railroad in the north end of the Great Salt Lake, Utah. (From Eardley, 1962, by permission of the Utah Geological Survey, Special Study 1.)

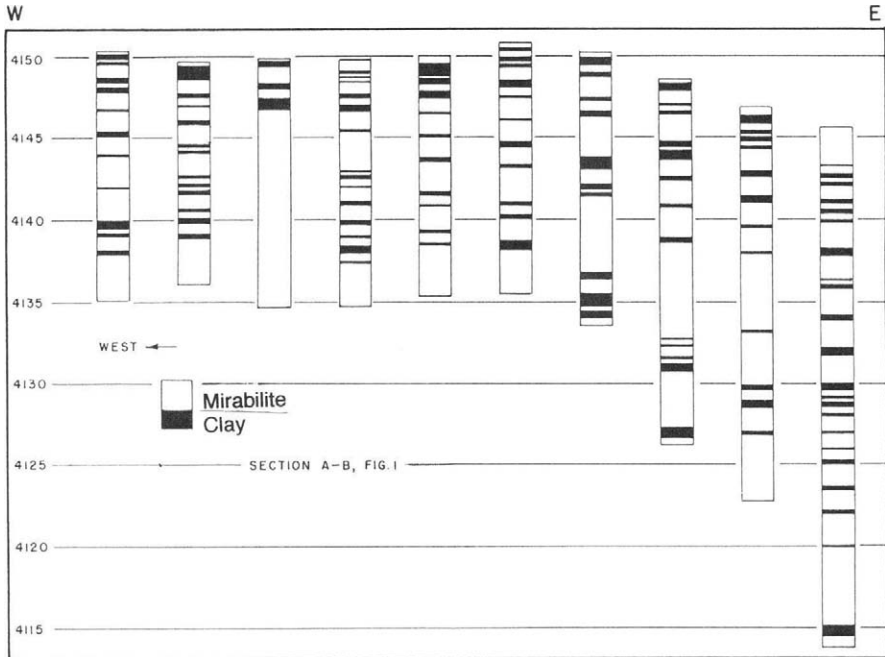


Figure 3.49 Stratigraphy of the Promontory Point mirabilite deposit, Utah. (From Eardley, 1962, by permission of the Utah Geological Survey, Special Study 1.)

layers, with the clay making up about 20% of the total mass (Fig. 3.49). Because of the superior strength properties of the mirabilite, it became the foundation for the rock-fill of the causeway. The mirabilite bed terminates abruptly at its point of maximum thickness near the shore, presumably because of being deposited against a sagging fault cliff. There is no knowledge of the extent of the deposit, but except for the clay layers it was very pure, containing only 0.1% Mg. Porewater in the mirabilite analyzed as 21.2% SO_4 , 23.8% Cl, 53.4% Na and 0.05% Mg, appearing to be spring-leached mirabilite, but still quite different from the present lake brine. The 23 clay interbeds (within the 9.8-m section) of mirabilite consist of 10–20% calcium carbonate and the rest clay minerals. They appear to be lenses, and not continuous layers. Radio carbon dating of the carbonates at the top of the bed indicate an age of 11,600 yr (Eardley, 1962).

Commercial Production

Various attempts have been made to produce sodium sulfate from the southeastern mirabilite bed. The initial method in 1920 involved first removing the 0.6 m of sandy overburden, and then injecting live steam into the deposit. This melted, dissolved and slightly agitated any broken mirabilite, allowing its sand content to settle. When a pool of saturated sodium sulfate had accumulated, it was pumped to a holding tank

to be further settled and decanted, and the clear brine pumped to cooling–crystallizer ponds. When full of mirabilite–thenardite the ponds were drained, the mirabilite allowed to dehydrate in place (during the area’s hot summers), and the product harvested. Two companies in succession attempted this method, and both failed (Wells, 1923).

A 23 mt/d pilot plant was constructed in 1934 in the southeast corner of the lake 26 km west of Salt Lake City, and successfully produced a 99–99.5% Na_2SO_4 , 0.5–1% NaCl product. Based upon this success a commercial plant was built and operated from 1939 to 1940 (Fig. 3.50; Wilson and Wideman, 1957). Their ore averaged 22.39% Na_2SO_4 , 1.53% NaCl, 0.47% MgCl_2 , 0.11% CaCl_2 , 45.70% insolubles, 26.70% water of hydration, and 2.80% moisture. It was 0.6–3 m thick, and covered by 0.45–1.2 m (average 0.6 m) of clean, spherical calcite sand (predominately 40–150 mesh in size). The overburden was first removed in a mining area, and holes 0.45–0.6 m deep were made in the mirabilite first by steam lances, and later by auger drills. Explosive charges were placed in the holes, and the ore was blasted. The broken ore was loaded by a gasoline-driven dragline into cars and hauled 0.4 km to the plant. There it was dumped

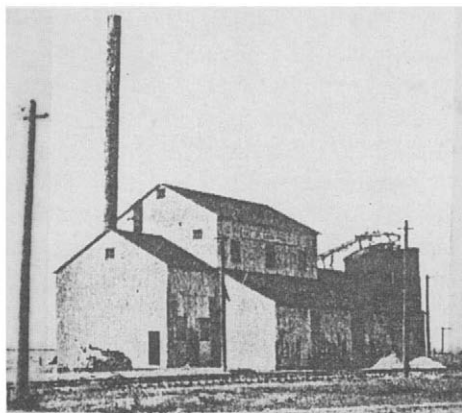
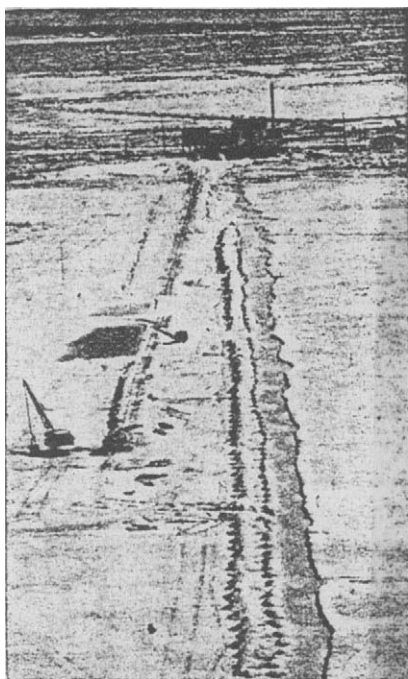


Figure 3.50 The sodium sulfate operation near the southeast corner of the Great Salt Lake. (From Martin, 1934, 1938, by permission of *Engineering & Mining Journal*.)

into a storage pile, to be later crushed in roll mills and loaded into steam-heated (to 65.6°C), agitated dissolving tanks with a 15-min residence time. At first the resultant slurry flowed into a 1.1-m-wide Akins classifier, and later a 1.5 × 4.9 m Dorr classifier that removed the sand and sent it to a tailings pile. The brine (its analysis as g/100 cc was 33.75 Na₂SO₄, 3.49 NaCl, 0.71 MgCl₂, 0.165 CaCl₂, 0.22 insolubles; pH 8.2) was sent to 4.9 × 5.5 m settling tanks for 24 hr, reheated, filtered, sent to surge tanks, and then to a triple-effect forced circulation evaporator heated by exhaust steam from the other process equipment. Slurry from the evaporator was settled in a 0.76 × 4.9 m Dorr classifier, and the thickened slurry centrifuged and washed in 1-m basket centrifuges. The cake was sent initially to a steam-heated rotary dryer, and later to a 1.2 × 5.9 m horizontal kiln dryer. Its discharge passed through 30 mesh screens, and then was sent to 200-t product storage bins. Steam was generated by a 250-HP, coal-fired Stirling boiler, and power (and exhaust steam) by Corliss and Ball engines. The product had an analysis of 97.94% Na₂SO₄, 0.78% MgSO₄, 0.57% NaCl, 0.35% CaSO₄, 0.15% MgCl₂, 0.04% insolubles, and 0.02% moisture (Martin, 1938, 1934). Other articles or studies on the GSL include those by Garrett (1965) and Anon. (1957, 1920).

Starting in 1970 the large solar pond potassium sulfate operation at the north end of the lake began producing sodium sulfate as a by-product, with an announced capacity of 136,000 mt/yr (Anon., 1972). In 1979 the capacity was said to be 45,000 t/yr (22,700–32,900 t/yr; McIlveen and Cheek, 1994), and production had been halted by 1993 (Anon., 1998). In 1984 their solar ponds flooded (because of a high lake level), and the production of both potassium and sodium sulfate was temporarily halted. Their first process had been stated to involve harvesting mirabilite from solar ponds in the winter, and then converting it to the anhydrous product with salt (Weisman and McIlveen, 1983). Later it was said to start with the cooling of concentrated brine from their solar ponds to crystallize mirabilite, and then evaporating it to form a much more pure anhydrous product.

Other Deposits

Many other playas in Utah contain a brine with a mixture of salts, including some sodium sulfate. *Sevier Lake* is one of the larger of these, with a saturated sodium chloride brine containing about 3% sodium sulfate, and a small amount of thenardite in its muds (Hampton, 1978; Whelan, 1969). A 5-cm crust of sodium sulfate was reported in its center in 1890, and a similar crust noted near Wendover on the western edge of the Salt Lake Desert. The latter sample contained 97.3% thenardite and “covered several acres” (~1 ha; Wells, 1923).

Wyoming

Wyoming contains many closed basin “alkali” playas and lakes, as well as alkali springs and wells. All of the playas contain mixed-salt deposits, but as with the

glacially formed lake/playa deposits in the western United States and Canada, Wyoming has many that contain dominant amounts of sodium sulfate, soda ash (trona $[\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot \text{H}_2\text{O}]$, or natron $[\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}]$), magnesium sulfate, or halite. Most of the playas or lakes are quite small (not including the gigantic buried Green River trona deposit, and the nearby subsurface brines).

Bull Lake

Several of the lakes have had commercial sodium sulfate production, such as Bull Lake in Carbon County, 40 km north of Rawlins. It is at an altitude of 2131 m and has an area of 33 ha (82 ac). It occurs in a shallow, closed depression in loosely consolidated sand and is underlain by massive shale. The region's temperature varies from -45 to $+38^\circ\text{C}$, the rainfall and snowfall are modest, and the winds blow frequently. The lake floods in the spring and maintains some brine in its deeper zones all year. There is a thin layer of mud over the entire surface of the lake, and under that a 0.8- to 8-m bed of mirabilite–thenardite. It contains thin interlayers of sand and mud, and in its lower section often becomes a mixture of mirabilite and sand. An average analysis of core samples was 56.5% Na_2SO_4 (22.3% of which occurred as thenardite; individual beds contained $\sim 97.7\%$ Na_2SO_4 ; see Table 3.26), 1.6% other salts, and 41.9% insolubles (on an anhydrous basis).

The initial operations at Bull Lake began in 1928 and continued past 1951 by the Iowa Soda Products Co., even though a fire destroyed their processing plant in 1947. The ore was drilled, lightly blasted in sections 2.4 m deep and 3 m wide, and then loaded into trucks by a small dragline power shovel with a clamshell bucket. In the plant the ore was dissolved in hot water and live steam (from an oil-fired boiler), and then pumped to one of five settling tanks. When clear the brine was decanted and pumped to one of two flat metal pans, 15.2 m long and 1.1 m wide. Here the brine cooled and evaporated, crystallizing a mirabilite–thenardite mixture. The crystals were continuously removed by a drag scrapper in the bottom of the pan, and conveyed to the top of a 12.2-m-high tower. There they dropped through a stream of steam-heated air, were gathered at the base, and dropped through the tower again. A fine powder analyzing as 96% Na_2SO_4 and 3.7% water was produced at a rate of 10 t per 8-hr shift. After the plant fire, the operation changed to one where strong brine was pumped from the lake to a smaller nearby lake to the south, and allowed to further evaporate and crystallize. It was drained in the late fall and harvested in the winter with a front-end loader, leaving a 0.3-m base of mirabilite to prevent contamination by the underlying mud. The harvested mirabilite was dumped onto drying pads and periodically turned until nearly dehydrated. It was then loaded into trucks, shipped to the railroad at Rawlins, and sold as a 10–15% H_2O cattle feed. The maximum annual production did not exceed 6000 t, and a total of 100,000 t had been shipped by 1951 (Young, 1951; Anon., 1951b).

Table 3.26
The Composition of Several High-Sodium-Sulfate Playas or Lakes
in Wyoming (wt%) (Schultz, 1909–1959)

	Na ₂ SO ₄	NaCl	MgSO ₄	Na ₂ CO ₃	CaSO ₄	Insol.
Big Sandy River ^{a,b}	86.44	13.56	—	—	—	—
Bull Spring (Bothwell) ^c	97.73	0.74	1.53	—	—	—
Bull Spring (Bothwell) ^{a,c}	93.87	3.09	3.04	—	—	—
Dillon ^c	88.92	2.35	8.73	—	—	—
Downey, North ^d	94.00	0.28	4.77	—	0.95	—
Downey, North ^{a,d}	85.38	—	4.80	—	—	9.82
Middle ^{a,d}	76.24	—	6.54	—	—	17.22
Gill ^e	94.50	0.54	2.52	—	—	2.44
Morgan ^e	94.33	1.56	—	4.11	—	—
New York ^{e,f}	81.70	7.21	—	11.09	—	—
Union Pacific Group ^b	94.23	3.14	2.63	—	—	—
Product ^{a,b}	95.30	2.36	2.34	—	—	—
Wilmington ^{e,f}	75.45	4.04	—	20.51	—	—

^aSchultz (1959).

^bFremont County.

^cCarbon County.

^dAlbany County.

^eNatrona County.

^fIndependence Group.

Gill Lakes

The Gill Soda Co. worked the Gill Lakes 13 km northeast of Casper in Natrona County. The principal deposit was 5.3 ha in size, dry most of the year, and had a mirabilite bed more than 6.7 m thick. The company mined the deposit with a clamshell bucket, and also operated a second lake 6.4 km east of Casper (as the Pratt Sodium Sulfate Co.), producing 3967 t of Na₂SO₄ in 1949. A spring flowing into this lake was estimated to discharge 1000 t of Na₂SO₄/yr. The company also owned a small playa 48 km northwest of Casper that contained an estimated 250,000 t of Na₂SO₄ and supplied mirabilite to the Columbian Hog & Cattle Co. (Tyler, 1935; Wells, 1923).

Other Deposits

The four *Union Pacific Lakes* (24 ha total area) located 21 km southwest of Laramie contained mirabilite beds 2.7–4.3 m thick under 1.1 m of mud (beds up to 12 m thick; Cole, 1926). From 1885 to 1892 they produced mirabilite by pumping strong brine from one lake (which could be up to 1.8 m deep in the spring) into a smaller one to more rapidly evaporate the brine and crystallize mirabilite. The mirabilite was then drained, harvested, partially air-dried, and shipped by rail (the Union Pacific Railroad built a spur track to the lakes) to the Laramie Chemical

Works for conversion into soda ash, caustic soda, and anhydrous sodium sulfate. The last product was made by dehydrating mirabilite in crude equipment, and one shipment to a glass factory analyzed as 96.37% Na_2SO_4 , 2.05% MgSO_4 , and 1.58% NaCl .

Other Wyoming playas that contained principally sodium sulfate included the *Bothwell Deposits* in Carbon County. The main deposit was only 229×457 m in size, with 0.6-m-thick mirabilite (which graded into thenardite in its lower section). It contained about 2% MgSO_4 and 1.8–4.2% insolubles, and the soil in the area also had a high Na_2SO_4 content. The three *Downey Lakes* in Albany County were 35 km southwest of Laramie and were in a 0.8×3.2 km depression. Their combined area was about 40 ha, the mirabilite beds were 0–3.6 m thick, and estimates of their reserves varied from 0.5 to 4 million t of mirabilite (an average analysis was 88.4% mirabilite, 5.4% epsomite, 6.2% insolubles; Schultz, 1909). *Holmes Lake* in Park County was located 4 km northwest of Cody, 2 ha in size, and contained beds of mirabilite. The *Independence Deposits*, Natrona County, included the New York and Philadelphia claims (44–65 ha) in the Berthaton group, with 0- to 6-m thick mirabilite containing 81.7% Na_2SO_4 , 11.1% Na_2CO_3 , and 7.2% NaCl . The *Morgan Deposit*, 11 km south of Split Rock in Natrona County, covers 65 ha and contains mirabilite beds up to 4.6 m thick analyzing as 94.3% Na_2SO_4 , 4.1% Na_2CO_3 , and 1.6% NaCl . *Split Rock Lake*, also in Natrona County, has 2.4 ha of “deep mirabilite” and 40 ha of thenardite crusts. The *Pacific Springs* deposit in Fremont County contained 82.23% Na_2SO_4 , 14.82% Na_2CO_3 , and 3.95% NaCl (Schultz, 1910).

In addition to the playas, there are many lakes and springs with a high Na_2SO_4 content, such as *Lake de Smet*, *Percy Lake*, *Pacific Springs*, and *Thermopolis Hot Springs* (Wells, 1923). The connected *Wilmington* and *Wilkesbarre* lakes are 65 and 8 ha in size, respectively, and contain a strong sodium sulfate brine (Anon., 1951b). Many other playas contain a mixture of sodium sulfate and sodium carbonate, such as the Omaha Soda Deposit, averaging 40.7% Na_2SO_4 , 54.9% Na_2CO_3 , and 4.4% NaCl (Garrett, 1992).

Other States

Several occurrences of sodium sulfate have been reported in *Colorado*, such as the four *Burdsalls Soda Lakes* 19 km south of Denver that had “sodium sulfate crusts around their margins” (Wells, 1923). Other high-sodium sulfate lakes and springs were mentioned in Jefferson and El Paso counties (Tyler, 1935). In *Idaho*, deposits of mirabilite mixed with epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) have been reported just west of Jump Creek in western Idaho (the *Claytonia* claims) and extending intermittently over a considerable area between Jump and Sucker Creeks (Wells, 1923). Tyler (1935) reported them occurring from Jump Creek westward into Malheur County, *Oregon*. Sodium sulfate minerals have also been reported in *New Jersey* (Hawkins, 1928, 1933), northeast *Ohio* (Connors, 1974), in some marine shales (Murata, 1977), and in various other locations (e.g., Smith, 1966; Anon., 1920).

MINOR DEPOSITS

Australia

There appear to be no large or small potentially commercial deposits of sodium sulfate in Australia. However, there are many playas, lakes, and brine sources with some to a modest sodium sulfate content, and various sulfate minerals occur in a number of locations. For instance, the permian Berry Formation of the Sydney Basin, New South Wales, contains some sodium sulfate (Goldbery and Loughnan, 1970), and elsewhere in southwestern New South Wales small mirabilite deposits have been noted in various playas (Sutton, 1982). There are also more than 100 playa lakes in the 120-km-long Karinga Creek drainage system of the Amadeus Basin in the Northern Territory (Fig. 3.51), which contain some soluble sulfates.

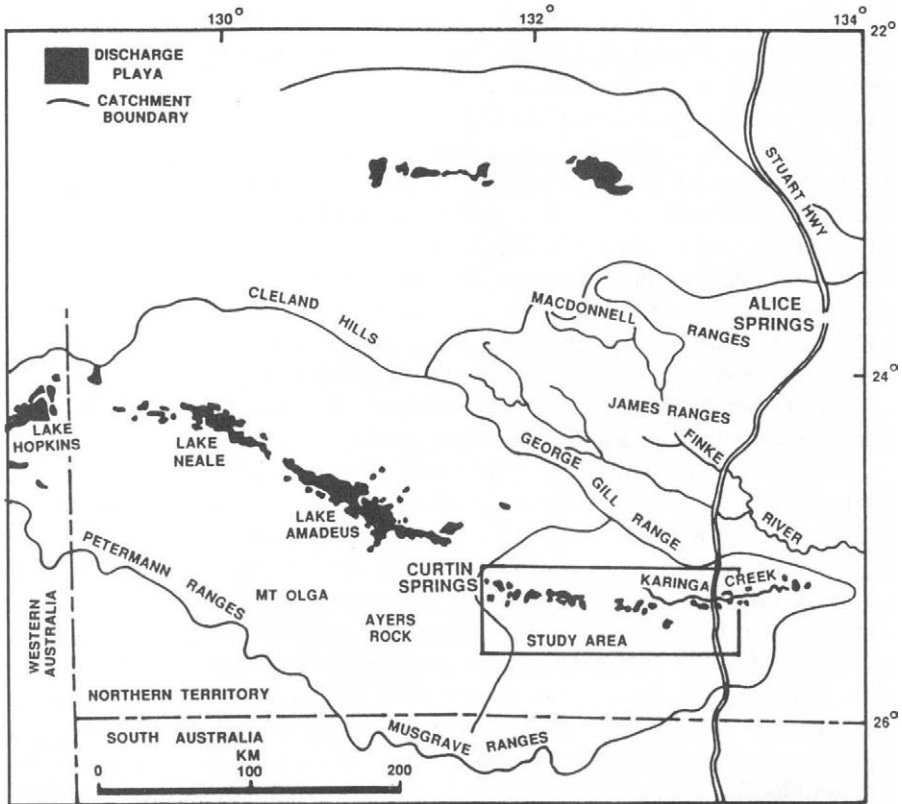


Figure 3.51 Location and drainage map of the Karinga Creek area, Australia. (Reprinted from *Sedimentary Geology*, Vol. 70, pp. 42–51, Arakel and Cohen, 1991, with permission of Elsevier Science.)

Table 3.27

Typical Water, Spring, and Lake Analyses of the Karinga Creek Playas, Australia (wt%)

	Na	Mg	Ca	K	Cl	SO ₄	HCO ₃ ^c	TDS	Density
Average playa ^a	7.05	0.57	800 ^c	0.32	12.15	2.79	81	22.96	1.14
Leached rock ^{a,c}	7580	362	1010	245	9700	2920	64	21900	1.02
Calc. ^d spring ^{a,c}	2230	287	416	178	3470	1800	168	8540	1.01
Calc. aquifer ^{a,c}	280	50	95	38	394	200	319	1376	1.00
Calatta Lake ^b									
Spring	4.11	0.19	615 ^c	0.26	6.66	1.60	272	12.91	1.091
Summer	10.42	0.39	353 ^c	0.40	15.73	3.04	138	25.50	1.178

^aArakel and Cohen (1991).^bArakel and Hongjun (1994).^cppm.^dCalcrete.

The average playa in the Karinga Creek has a surface crust in the summer that usually is only a few centimeters thick and contains halite (NaCl), glauberite (Na₂SO₄·CaSO₄), thenardite (Na₂SO₄), and mirabilite (Na₂SO₄·10H₂O). In this arid land the annual rainfall averages 226–333 mm and the potential evaporation 3000 mm: the average monthly maximum temperature is 33°C in January and the average minimum 4°C in July. The predominant rock in the drainage basins is calcite conglomerates (“calcretes”). The summertime vadose zone under the playas is <1 m thick, and the phreatic (brine-filled) zone 0.5–2.5 m, with the salt content in the interstitial brine up to 200 g/liter (see Table 3.27; some surface brines can reach 450 g/liter). Gypsum is the dominant precipitated mineral in the playa sediments, and glauberite the second most common sulfate mineral. Thenardite and mirabilite are also frequently present, along with astrakanite (Na₂SO₄·MgSO₄·4H₂O) in the playas in the high-magnesium eastern end of the system.

The glauberite in the phreatic zone occurs as nodules a few centimeters in diameter, and/or lensoid assemblages of coarse crystals 5–20 cm thick and several decimeters long (Fig. 3.52). The individual crystals in these groupings are up to a few centimeters long, euhedral, and usually free of inclusions. Their orientation is random to oriented, and occasionally they are aligned around the nodule walls. The nodules or lens clusters have an average of 15% loose gypsum crystals in their centers. It would appear that the glauberite in this zone formed by direct precipitation from high-sodium-sulfate brines contacting high-calcium groundwater. However, the average brine (as indicated in Table 3.27) is not strong enough for this reaction, so mirabilite or thenardite must have reacted directly with the groundwater, or dissolved to locally form areas with an adequate sodium sulfate concentration.

In the quite moist (up to 25% water) vadose zone the glauberite is seen replacing gypsum crystals or clusters, starting at the edges, then the faces, and gradually penetrating into the interior. The individual glauberite crystals in this replacement

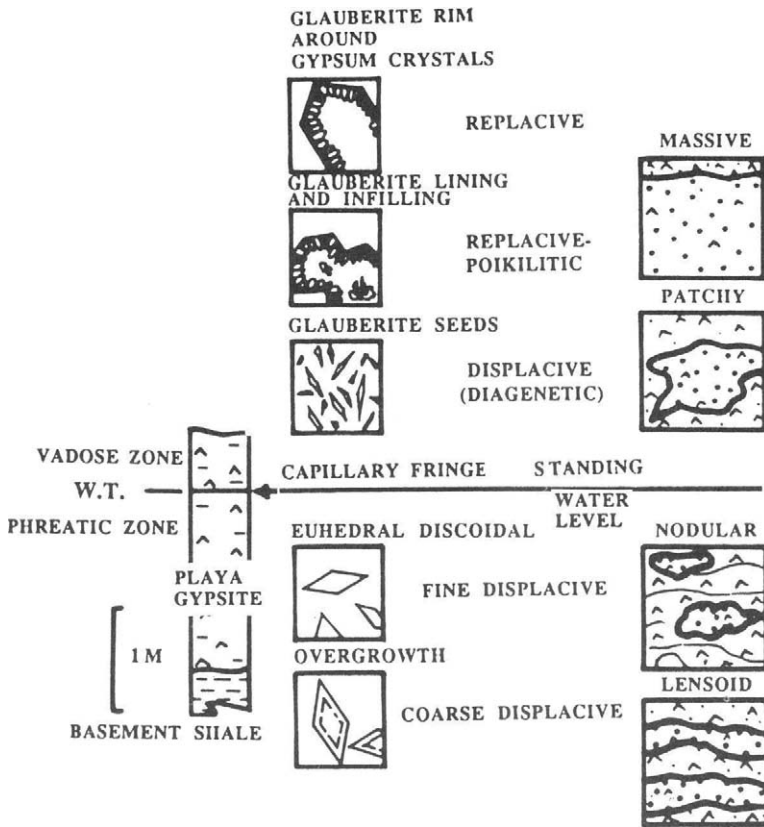


Figure 3.52 Glauberite crystal structures found in the Karinga Creek playas. (Reprinted from *Sedimentary Geology*, Vol. 70, Arakel and Cohen, 1991, pp. 42–51, with permission of Elsevier Science.)

zone are 0.2–0.8 mm long, tightly packed, and perpendicular to the face of the gypsum. Thenardite is also usually present in the vadose zone in the summer, and mirabilite can be assumed to have been present both here and the phreatic zone in the winter (Arakel and Cohen, 1991).

More detail has been given on one of the sulfate playas in this area, Calatta Lake, which crystallizes halite, followed by thenardite, on its surface in the summer. In the winter alternating layers of halite and mirabilite are formed on the surface, and mirabilite beneath the surface. All of the salts in the surface crusts dissolve when flooded in the spring. Most of the lake's entering drainage water has contacted calcrete, shale, or gypsite rocks, and the lake sediments include 10 cm of silty-to-sandy clay on the surface that blends into an underlying red clay. These sediments contain variable quantities of any or all of halite, gypsum, glauberite, mirabilite, thenardite,

epsomite, and polyhalite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Examples of the playa's brines are given in Table 3.27 (Arakel and Hongjun, 1994).

Botswana

A large playa lake in Botswana is somewhat typical of the immense number of playas or lakes in the world that contain brines with a mixture of salts, and where the commercial recovery of one salt improves the potential for also producing sodium sulfate. In this case a large (300,000 t/yr) carbonation plant was built in 1990 to recover soda ash from the subsurface brines of the Sua (or Sowa) Pan playa, and the initial plans were to also recover sizable amounts of salt (650,000 t/yr) and sodium sulfate (100,000 t/yr) as by-products (as of 1999 the sodium sulfate production had not yet started). The area is fed by the Nata River from the east, and the Okavango River (through the Okavango Swamp) from the west flowing into the large 200×120 km Makgadikgadi playa. The Sua Pan is the most easterly section of this playa, about 180 km southwest of Francistown. The area has a short, dry winter (average 400 mm/yr rainfall, 5°C minimum temperatures in July) and a long, hot summer (daytime average 32°C in January). The pan has a flat-lying surface at an altitude of 890 m, and a 30-m-thick, $>915 \text{ km}^2$ aquifer zone of porous sand, overlain by sand and clay (Fig. 3.53). The brine in the aquifer averages (as g/liter) about 128.0 NaCl, 23.1 Na_2CO_3 , 9.6 NaHCO_3 , 13.8 Na_2SO_4 and 4.3 KCl. Its density is 1.124 g/cc, the pH 9.13, and presumably there are about 110 million t of Na_2SO_4 in the brine. About 55 wells, 35 m deep, pump brine to solar evaporation ponds to concentrate it and crystallize halite (which is harvested), allowing the final brine to be carbonated to crystallize NaHCO_3 . Mirabilite was planned to be recovered by cooling the residual brine, as at Searles Lake (Garrett, 1992; Anon., 1984a).

Brazil

Only a few sodium sulfate lakes or playas have been reported in Brazil, despite the country having some arid plateau areas. One of these deposits is Sete Lagoas, a group of seven small playas <5 ha in size and totaling 30 ha. They are fed by four hot springs ($36\text{--}38.5^\circ\text{C}$ water) flowing through sandstone and conglomerate formations. The lakes accumulate $>200 \text{ m}^3$ of brine in the spring, which totally evaporates by May to August, leaving 3–30 cm of surface salts. A typical composition of these crusts is 55.82–63.35% Na_2SO_4 , 0.85–1.50% NaCl, 2.55–4.68% CaSO_4 , 1.50–2.50% MgCl_2 , and 26.97–39.28% insolubles. Small amounts of the salts had been harvested for many years as a cattle food (Freise, 1932).

Europe

Many occurrences or small deposits of sodium sulfate minerals have been reported in various European countries. For instance, in *Bulgaria* glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$)

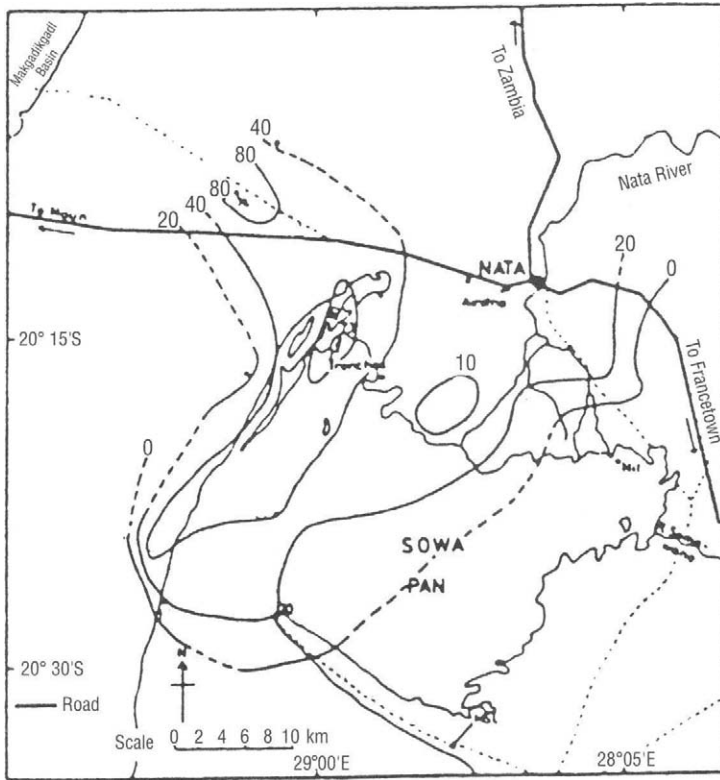


Figure 3.53 Concentration map of sodium carbonate found in the aquifer brine of the Sua Pan (g/liter). From Garrett, 1992.

is found near the alkaline mineral springs in the Sofia area (Shterev, 1969). In *Germany* there is also considerable glauberite near the weakly mineralized high-sulfate springs near Bunter on the eastern margin of the Black Forest (Kaess, 1967), and at Stubensandstein Wuertemberg (Frank, 1952). Glauberite and other sulfate minerals are also common near some fumarolic springs, such as in *France* and *Italy*. In the latter country various soluble sulfate salts (astrakanite [$\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$], glauberite, burkeite [$2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$], and thenardite [Na_2SO_4]) have also been reported in volcanic areas such as near Mount Vesuvius (Alfani, 1935) and the Vulcano Island (Garaveli *et al.*, 1997). Similar deposits have been formed by the fumaroles on *Reunion*, in the West Indies (Nativel, 1972). Mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and thenardite may also be found in caves, such as in *Northern Ireland* (Kelly and Fogg, 1997). Lacu Sarat lake, *Romania*, 16–19 km south of Braila on the west shore of the Danube River, forms glauber salt deposits in the winter (Wells, 1923).

India

By-Product: Didwana Salt Pans

There are many small sodium sulfate deposits and occurrences in India, although apparently no large deposits. There are 248 saline lakes containing sodium sulfate in the Sind district alone, the state of Rajasthan has many more, and there are many areas with a high-sodium-sulfate soil. There has also been some recovery as a by-product from salt production, such as at the 15.5 km² *Didwana* playa in Rajasthan. It contains a high-sodium chloride/sulfate subsurface brine that was used to produce an average of 13,000 t/yr of salt, while a separate layer of thenardite crystallized under the salt. Brine was pumped during the summer from a depth of 4.5–6 m into 250 small solar ponds made by scraping the sandy-silt playa surface to form 26 × 37 m pits with a 1-m wide, 0.6-m high ridge between adjacent ponds. The brine feeding the ponds averaged 18.5% NaCl, 6.6% Na₂SO₄, and 0.8% Na₂CO₃, and the salt product contained 87.2% NaCl, 11.2% Na₂SO₄, 0.3% Na₂CO₃, 0.64% insolubles, and 0.66% H₂O. Over the 150 or so years that the ponds produced salt a 250,000 t, 0.6- to 1-m thick bed of fairly pure thenardite accumulated. It was eventually mined, giving a product averaging 91.7% Na₂SO₄, 0.80% NaCl, 0.50% Na₂CO₃, 0.24 CaSO₄, 0.30% MgSO₄, 0.20% H₂O, and 6.26% insolubles. The thenardite was primarily in the form of interlocking masses of 0.6 to >2.5 cm orthorhombic, pyramidal crystals, with some crystals 5–8 cm in size and perfectly clear (Fig. 3.54; Spencer, 1944, 1943).

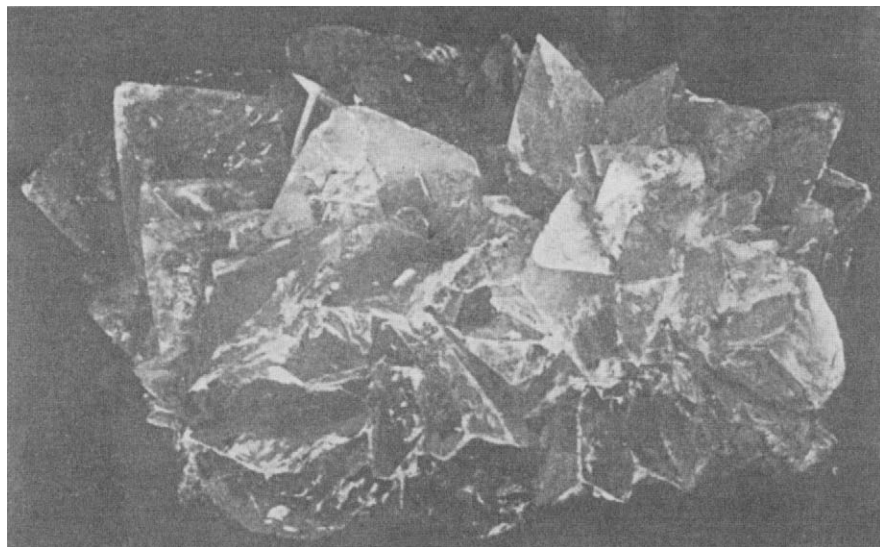


Figure 3.54 Thenardite crystals formed under the Didwana salt ponds, India. (From Spencer, 1944, by permission of the Mineralogical Society.)

Later the average NaCl/Na₂SO₄ ratio in the brine changed to 3–4/1, and the brine contained an estimated 1.8 million t of sodium sulfate. A process to recover both salt and thenardite was then inaugurated. Pits were dug into the lake bed as before, and the brine that collected in them was pumped into solar ponds to initially deposit salt during the hot summers. Thenardite of a 90–96% purity and containing only a small amount of sodium chloride, sodium carbonate, sand, and a dark greenish clay could then be crystallized by the initial evaporation of the residual brine. A second 10,000–15,000 t/yr harvest was then formed before the brine seeped away, containing 7–12% NaCl, and sold as a lower-grade product or redissolved and re-evaporated (Sapre, 1956).

Sambhar Lake

Sambhar Lake is a large producer of salt, and its bitterns (residual brine) represents a potential source of 22 million tons of Na₂SO₄. Typical percentages of the salts in the lake brine are 87.9% NaCl, 7.2% Na₂SO₄, and 4.8% Na₂CO₃; in the interstitial brine in the lake floor, 78.9% NaCl, 14.3% Na₂SO₄, and 6.8% Na₂CO₃; and in the bitterns, 66.0% NaCl, 21.3% Na₂SO₄, and 12.6% Na₂CO₃. However, sodium sulfate has never been recovered from the lake, and for more than 140 years the bitterns from the salt operation have been impounded in the adjacent East Lake (Sapre, 1956). This lake is unusual in containing six strains of the *Natronbacterium* genus, which can only live in brines with >15% NaCl and a pH >9 (Upasani and Desai, 1990).

Tsokar (Tso-Kar) Lake

Tsokar Lake is 125 km southeast of Leh in the Ladakh district of the Himalayan Mountains in Kashmir. It is at an altitude of 4572 m and has an area of 20 km² (4480 m and 17.5 km² [7 × 2.5 km]; Kashkari, 1984). The climate is arid, with winter temperatures reaching –20°C, and the permanent permafrost in the area is at a depth of ~2 m. The lake appears to have been formed in the Pleistocene by glacial scooping and has ancient shorelines 60–70 m above the present lake surface. It is fed by several seasonal and perennial streams, with some water from geothermal springs. The lake's brine analysis is 8.48% SO₄, 6.73% Cl, 0.52% B₄O₇, 5.00% Na, 1.87% K, and 1.31% Mg. A shallow drilling program found extensive zones (61) around the dry exterior of the lake with buried near-surface mirabilite–thenardite deposits 0.2–2 m thick, with an average analysis of 81.29% Na₂SO₄, 0.57% Cl, 2600 ppm B, 250 ppm NO₃, 3.16% K, 0.45% Mg, 0.39% Ca, and 14.14% insolubles. Some individual lenses contained up to 15,800 m³ of thenardite, and the total deposit (including the brine) was estimated to contain 1.06 million mt of Na₂SO₄. Several studies have been made on the recovery of sodium sulfate and other salts from the lake (Dhar *et al.*, 1987; Kashkari, 1984; Anon., 1984b; Varma, 1972).

Sind Area

The analysis of the brine in various of the Sind area lakes in India, as g/liter of Na₂SO₄ and then Na₂CO₃, are Barko, 11.2 and 98.6; Gadanwari, 3.8 and 27.6; Ganjawari, 24.7 and 72.1; Khariri Mojanwari, 21.5 and 78.4; Lambro, 37.2 and 13.4;

Mithri, 55.3 and 124.0; Pakhyaro, 4.0 and 74.2; Rait Pario, 6.6 and 5.5; and Sukchaho, 26.3 and 0 (Sahni, 1951).

“Alkaline” Soils

High-sodium-sulfate soils (called “reh”) occur over large areas of India, such as an estimated 166 km² in Uttar Pradesh containing perhaps 106,000 t of sodium sulfate, and during the 1950s about 20,000 t/yr of Na₂SO₄ were produced from them. Examples of their analyses are Moradabad, 8.66% Na₂SO₄, 9.66% Na₂CO₃, 8.55% NaHCO₃, and 1.92% NaCl; and Meerut, 1.19% Na₂SO₄, 4.68% Na₂CO₃, 3.96% NaHCO₃, and 3.88% NaCl (Garrett, 1992).

Iraq

Several sodium sulfate deposits of potential commercial size are said to occur in Iraq, with the largest being the Shari Salt Lake. Studies have been made on the possible production of sodium sulfate from them (Jassim, 1993).

Kenya

There are many sodium carbonate/sulfate-containing lakes in Kenya and throughout the Rift Valley. A few also contain appreciable (and potentially commercial) deposits of sodium sulfate minerals (primarily burkeite [2Na₂SO₄·Na₂CO₃]), such as *Lake Katwe*, with 2 million mt of Na₂SO₄ (including some hanksite [9Na₂SO₄·2Na₂CO₃·KCl]; Garrett, 1992).

Mali

Five large and five small saline playas in the Taoudenni–Agorgott basin of northern Mali contain a high percentage of glauberite (Na₂SO₄·CaSO₄). They were formed by active lakes during the period 3000–8000 ybp, but since then the climate has been very dry, with about 10 mm/yr rainfall, average maximum summer temperatures of >40°C, and >20°C in the winter. The upper 16 cm of the playa surfaces consist of mud with gypsum formed by the leaching of glauberite, and the next 84 cm is rich in glauberite. There is then a thick halite layer, and under that glauberite beds of various grade and crystal size interlayered with thinner halite beds. Near the base of the soluble salts are a few layers of thenardite, some of which contain small amounts of astrakanite (Mees, 1998; Canals-Sabate *et al.*, 1990). Several dry lakes in northern Mali also contain small thenardite deposits.

Peru

A large zone (4.4 km² in area) of mirabilite occurs in the 14 km (E–W) by 8 km (N–S) Laguna Salinas of southern Peru (Figs. 3.13 and 3.55). This playa-lake is

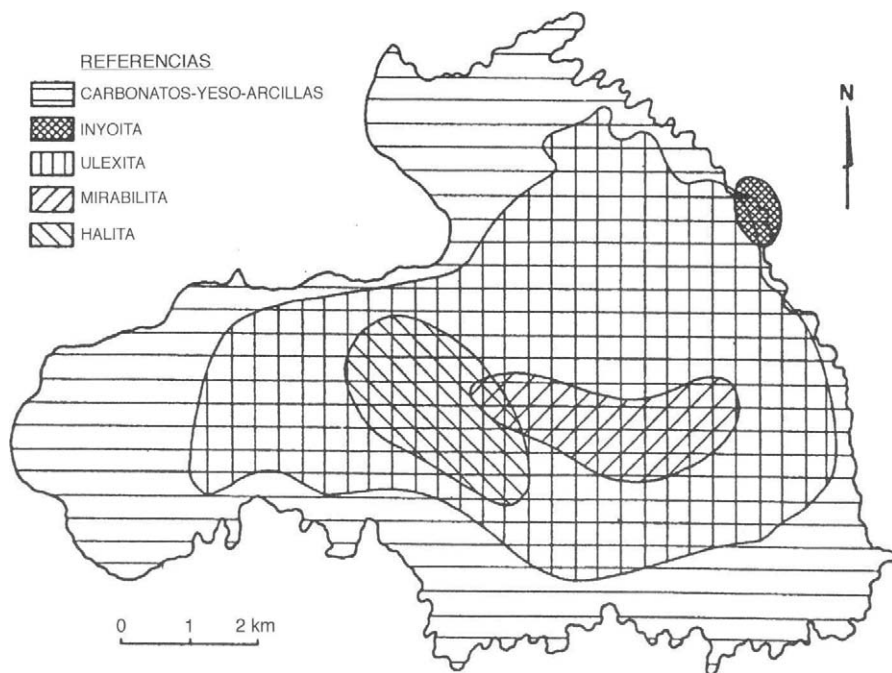


Figure 3.55 Mineral zones in the Laguna Salinas, Peru. (From Alonso, 1996, courtesy of the Asociación Geológica Argentina.)

80 km east of Arequipa at an altitude of 4200 m, in an arid-climate closed basin somewhat surrounded by high mountains (reaching 5400–5800 m) and fed by thermal springs and internal drainage. It becomes partly flooded (up to 50 cm deep) after the winter rains (December–March), and dries rapidly to form surface crusts containing mirabilite, thenardite, halite, and ulexite ($\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$). Beneath the surface in a 40 km² area there are irregular beds 0.5–2.7 m thick and clusters of nodules of ulexite, and in one 0.5 km² area inyoite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 13\text{H}_2\text{O}$). Ulexite has been recovered periodically from the salar since 1883 (by hand picking the ulexite nodules and slabs from narrow trenches). There are an estimated 20 million t of 27% B_2O_3 ulexite in the playa, making it one of the largest ulexite playas in the high-Andes (Puna) region. It probably also has the largest reserves of lithium (in its brine) and sodium sulfate in Peru.

In about the center of the playa is a 5 km² area of fairly pure halite, and adjacent to it to the east is an area of mirabilite–thenardite, containing about 3 million t of Na_2SO_4 . The sodium sulfate deposit has about equal amounts of thenardite and mirabilite (71.1% Na_2SO_4 and 0.05% NaCl) and often occurs in lenses 100 m by 1 m thick located between zones of ulexite beds and nodules. There are usually additional sodium sulfate efflorescence salts in the surface crusts above the sulfate area

(Alonso, 1996, 1995). High-sodium-sulfate soils have also been reported in certain other areas of Peru (Mees and Stoops, 1991).

South Africa

There are many alkali lakes and playas ("salt pans") in South Africa that contain brines with a mixture of salts, such as the *Britten* and *Hagenstad pans*. Some contain mirabilite–thenardite deposits and a high-sulfate brine (such as 10–20% NaCl, and 1–10% Na₂SO₄; Shuttleworth, 1963), but as of 1999 there was only modest sodium sulfate production from these lakes. However, a very interesting example of potential sodium sulfate recovery as a by-product from inland solar salt operations has been given by Sutherland (1993). He noted that Industrial Salt (Pty) Limited produces salt from a number of playas that are 10–50 km² in size. They contain subsurface brine at an 18–25°Be density that is nearly saturated with NaCl, and 20–25% of the dissolved salts are sodium sulfate. At Grootwitpan near Upington the brine analysis is, as g/liter; 230 NaCl, 51 Na₂SO₄, 2.1 Na₂CO₃, 0.1 Ca, and 0.01 Mg. Their solar ponds are 0.5–3 ha in size, the brine is maintained in them 100–150 mm deep, and a permanent layer of salt is left on the floor to prevent mud pickup during harvesting. After the brine has been pumped to the ponds and partly evaporated, salt crystallizes during the day and mirabilite crystallizes in the evenings (most heavily in the spring and fall), forming layers in the salt. If harvested in that condition the salt would contain 20–30% Na₂SO₄ and be unusable. However, it has been found that after the ponds have been drained for harvesting, if they are allowed to become dry and stand empty for a short period, the interstitial brine becomes heated, melting and dissolving much of the mirabilite. The resultant heavy brine (when first heated it has a 1.334 g/cm³ density compared to the NaCl brine's 1.275g/cm³) then seeps to the semi-impermeable mud under the (permeable) salt floor, where thenardite crystallizes after the brine has been further evaporated by capillary action, and becomes even hotter because of the trapped solar radiation. Over a relatively short period this layer of thenardite has grown to a thickness of about 0.5 m, and it analyzes as 90–95% Na₂SO₄ and 3–5% NaCl (this phenomenon is similar to that found in the salt ponds of Didwana, India). In South Africa the residual salt in the ponds can then be harvested (during 7 months of the year) and washed to reduce the Na₂SO₄ from 11.5 to <1.6% (with an 87.5% NaCl yield) to obtain a product with 98–99% purity.

Other Countries

In *Angola* high-sodium-sulfate thermal springs that have deposited sodium sulfate salts occur in the Cuanza Sul district (Figueiredo and Faria, 1972). High-sodium-sulfate brines and various sodium sulfate minerals have also been reported in the Tibesti area of *Chad* (Gac *et al.*, 1979). Thenardite has been reported in the Punjab region of *Pakistan*, and as in India, there are extensive regions with a highly

saline soil. Some of this sodium sulfate has been recovered as a cottage industry by leaching and then recrystallizing the alkaline soil (Shahid and Jenkins, 1994). Mirabilite has also been reported in the sebka (playa) sediments of southeastern *Tunisia* (Stengele and Smykatz-Kloss, 1995). One of the earlier recorded production operations for sodium sulfate occurred in the El Tocuyo and Quibor valleys of *Venezuela*, starting in the 16th century. A highly alkaline soil was leached, and a crude sodium sulfate crystallized as a salt substitute, an operation that continued until marine solar salt operations were established by the occupying Spaniards (Urbani and Salazar, 1995).

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CURRENT AND PRIOR COMMERCIAL OPERATIONS

The processing of natural sodium sulfate has undergone a transition over the years of two different types. Initially it was often produced from comparatively small deposits on a limited scale, while now predominantly large deposits are employed, and the production capacity of the average plant is very high. Also, initially the simplest equipment and procedures possible were employed, and the production of a slightly lower quality product was acceptable, whereas now the market is very competitive and most of the plants have become highly sophisticated and very efficient, and produce a high-quality product. There is still some production being practiced in the earlier mode to satisfy local needs, but most of the world's production is now recovered from the largest of the deposits, and well over 95% is produced in large, efficient plants. Some of the earlier processes have been briefly described in the geology chapters, but many others, as well as the newer operations and some of the developing technology, will be discussed in the following section.

Argentina***Sociedad Minera Pompeya S.A.***

The interior Andes Mountain "Puna" region of South America is a large, arid, very high plateau in the northwest corner of Argentina, the northeast corner of Chile, the southwest corner of Bolivia, and the southeast corner of Peru. There are many closed basins with saline playas and lakes in the region at an elevation of 3500–4000 m, and some have massive deposits of mirabilite and other salts. Lesino *et al.* (1990, 1982) have described an interesting application of salt-gradient solar ponds in the pilot plant production of sodium sulfate from one of these remotely located (but with inexpensive labor) salars. Four 20 × 20 m, 2.3-m deep leaching ponds were built and lined with 10-mil black polyethylene film that had thermally joined seams. A fifth rectangular crystallizer pond was also built and lined, with an

area of 550 m² and a 0.5-m depth. The ore to be used in the process averaged 75% mirabilite (Na₂SO₄·10H₂O; some as low as 68% Na₂SO₄ [dry basis]), 15% halite (some at 6%), and 10% mud (some at 25%). It was placed in the leaching ponds to a depth of 0.3 m and covered with 0.5 m of water. The solution that was formed was circulated by an external pump for 4 days until moderately concentrated at a density of 1.10 g/cm³, and then freshwater was slowly distributed during a 24-hr period over the pond's brine, in such a way as to cause the minimum mixing of the two layers. This formed the "salt gradient" condition, where the upper layer of water acted as a lens and thermal insulator for the absorption of solar energy in the lower brine layer. After 12 days (in the summer; 18 in the winter) the lower brine layer had reached a temperature of 40°C, was nearly saturated with sodium sulfate, and had a density of 1.32 g/cm³. It was then carefully pumped (so as to not pick up mud from the bottom or become diluted with the cover water) into the crystallizer pond where clean mirabilite (averaging only 0.13% NaCl on a Na₂SO₄ basis) formed in the cold evenings of the area. This was harvested and the brine returned to the salar. New mirabilite ore was then loaded into the salt-gradient pond, the former cover water was circulated to become the brine, and the process was repeated. Eventually when the residual mud was too thick, the ponds would be cleaned and the mud discarded. Plans were also underway to form new clean mirabilite-to-thenardite (Na₂SO₄; mirabilite dehydrating) salt-gradient ponds. In 1986, 777 t of mirabilite were produced by this method.

Canada

As noted in the geology section, there has been continuous production of sodium sulfate from one or more of Canada's numerous playa/lake deposits for more than 80 yr. During this period more than 25 different lakes have been worked, and at the peak of production there were seven large operations (in 1976; see Fig. 3.6). However, with increasing competition and the need for lower cost production with a higher quality product, by 1999 only three were still in production. A review of some of the earlier as well as the current operations supplies an excellent history of the industry, since many of the changes and innovations of both equipment and processes that took place in Canada mirror the actions of the entire industry. Several of these operations will be discussed below, alphabetically by the lakes and by the sequence of process developments that took place as they attempted to develop a lower cost, trouble-free process that produced a high-quality product.

Alask and Frederick Lakes (Natural Sodium Products Ltd.)

The initial processing of sodium sulfate in Canada started in 1918 and was by the simple harvesting of the comparatively pure (but thin) autumn-formed ("intermittent") surface salts, or by mining surface layers of mirabilite crystals when they were fairly clean. The first more substantial operation took place at Frederick Lake from 1921 to 1955, where the near-surface bedded deposits were blasted to a depth

of 1.5–1.8 m (Fig. 4.1), and then the loosened mirabilite was loaded and hauled to a washing plant or stockpile by a four-car diesel train (each car held 3.8 m^3 [5 yd^3]). Some ore could also be mined without blasting by a 1.1 m^3 (1.5 yd^3) shovel, and later additional mirabilite was formed in ponds and harvested by tractors and scrapers.

In the washing plant, vigorous agitation in a log washer (Fig. 4.2) with a saturated sodium sulfate brine loosened and removed some of the insolubles, and the brine dissolved part of the other soluble salts. A constant bleed stream was removed, thus improving the product's purity and consistency. Dehydration and drying of the washed and drained mirabilite was done in four 2.1-m diameter, 24-m long oil-fired rotary dryers, but the operation was difficult and the purity further reduced. Over-sized product was passed through a hammer mill before being sent to the storage silo. The product was very dusty, off-color, and usually only contained 94–96% Na_2SO_4 , but the operation was simple and inexpensive, the plant cost was fairly



Figure 4.1 Glauber salt cooling ponds, and natural mirabilite surface in Canada. *Upper left:* Cooling ponds. *Upper right:* Glauber salt surface after draining. *Lower left:* Blasted mirabilite ore bed at Frederick Lake. *Lower right:* Windrowed glauber salt in pond. (From Rueffel, 1976, courtesy of the National Research Council of Canada.)

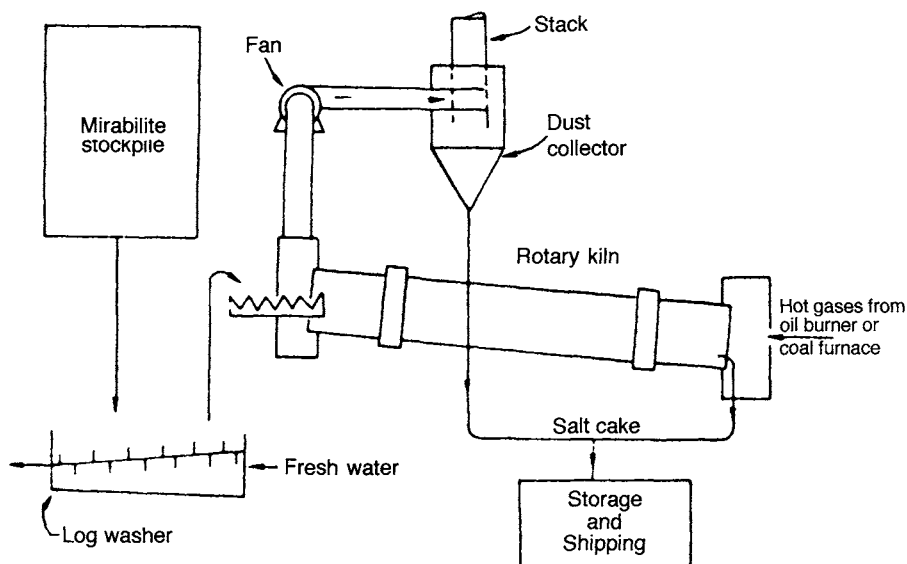


Figure 4.2 Mirabilite ore washing, rotary dehydration-drying process. (From Broughton, 1976, courtesy of the Montana Bureau of Mines and Geology.)

low, and it could be done on a year-round basis if the lake floor was firm. A similar process was used at Alsask Lake by the same company from 1942 to 1944, also employing four large kilns (Rueffel, 1976; Tomkins, 1954).

Chaplin Lake (Saskatchewan Minerals)

The first of the higher purity processing systems to be used in Canada was called “brining.” Chaplin Lake does not have permanent salt beds, so brine has always been used as its feed material. A 26-km² freshwater holding basin (Fig. 3.7; called Miller’s Lake) was built to receive much of the spring runoff from the surrounding area and allow a more controlled flow to Chaplin Lake (a similar reservoir was also built at their Frederick “Bishopric” Lake operation, which was very similar to that at Chaplin Lake). Initially, deep artesian water wells were also used to supplement the amount of water in the lake, but since the well water was warm and highly mineralized (sufficient to be used in a spa at nearby Moose Jaw), natural flow alone was later utilized (occasionally leading to water shortages). Chaplin Lake was also subdivided, with the east section (locally called “East Chaplin Lake”) having a potential flooded area of 13 km². The western segment (“West Chaplin Lake”) had an area of 31 km², four internal subdivisions, and apparently more mirabilite in its bottom mud. Weirs, pumps (with 5500–12,000 gpm capacity), and 4.8 km of canals were also built, and located to control the flow of water from the reservoir, and brine to and from each of the lake sections.

As operated in 1999, if not already supplied by the local runoff, each lake section is flooded with 10–15 cm (4–6 in) of lake water in the spring to concentrate and, ideally, dissolve some mirabilite from the mud floor. During the summer additional lake water is primarily added to East Chaplin Lake, and its intermediate-strength brine sent to the first section of West Chaplin. When the last section's brine reaches a concentration of at least 16% Na_2SO_4 (initially the cutoff was 20–25%), it is sent through a canal to three 51 or 61 cm (20 or 24 in) centrifugal pumps. The pumps then route it to five (originally three) 100×100 m (12 ha), 3.3–4.5 m deep ponds (each with a 300 million gallon brine capacity) near the plant to be held until the weather turns cold. The salts in the brine in 1999 were in the ratio of (on a dry basis) $\sim 70\%$ Na_2SO_4 , $\sim 20\%$ MgSO_4 , and $\sim 10\%$ NaCl , with this ratio having only slightly changed since the operation began in 1947. On particularly warm summers the concentrating process can be repeated several times in one year to fill the ponds with up to 3.3 m (10 ft) of brine (e.g., there were three concentrating cycles in the very warm summer of 1998, producing 400,000 t of glauber salt). In the autumn and early winter 1.3–2 m thick beds of mirabilite usually crystallize in these ponds, and in early November the residual brine is drained from them and discharged into canals flowing back to the northern edge of West Lake. Retaining boards 0.3 m (1 ft) high in weirs in the pond walls are removed (from the top downward) in succession to cause a gentle flow that carries away the minimum amount of glauber salt.

After draining, when the ponds have become fairly dry, the surface is windrowed to allow further drainage and assist in the later harvesting. This also reduces the later crystallization (in the very cold winters) of ice and the brine's other soluble salts (such as astrakanite [$\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$], epsomite [$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$], and sodium chloride dihydrate [$\text{NaCl} \cdot 2\text{H}_2\text{O}$]). The final glauber salt with its entrained brine contains about 30% Na_2SO_4 and 3.78 t of it were required in 1999 to produce 1 t of anhydrous sodium sulfate. During the winter it is harvested by contract excavators using conventional earth-moving equipment, with about a 30-cm layer of glauber salt being left in the ponds as a clean floor (Fig. 4.3). It is hauled to the plant and formed into a large ($>250,000$ t) stockpile (Fig. 4.4) for year-round processing.

In the initial pant the mirabilite was dehydrated without further processing by passing it through long (1.8–2.4 m diameter, 24–34 m long) rotary dryers (Fig. 4.2) with a large, loose chain inside to help prevent caking as the glauber salt melted. The mirabilite was fed into one end, and flue gas from the burning of lignite or heavy oil entered at the other. As a slurry formed near the front end (from glauber salt being melted) it tended to plug the unit as it contacted the drier solids near the center. The uneven movement of the chain helped to dislodge the wet, sticky paste that was formed, but extreme skill was required by the operators, and frequently the dehydrator–dryer still plugged, or a flow of slurry would suddenly come out the product end. When either event occurred the dryer had to be shut down, cooled and then manually cleaned, consuming a great deal of time and expense, averaging at least 12–16% lost time and production. The dried product tended to be either powder (2–3 t of dust loss in the stack per 50 t of product, with often 12–15 cm of dust



Figure 4.3 Harvested glauber salt cooling pond at Chaplin Lake, Canada. (Courtesy of Saskatchewan Minerals.)

on the floor) or somewhat granulated (i.e., in small balls) and gray in color from the organics in the glauber salt, or from the oil or lignite fire. Also, the production rate was very slow and the fuel efficiency was poor. However, the capital cost was comparatively low, the operation was simple, and it was well suited to this early period when the plants were small, there was limited competition, and the product specifications were not demanding (since most of it went to the kraft paper mills and was immediately sent to waste-liquor burners). The plugging problems in the

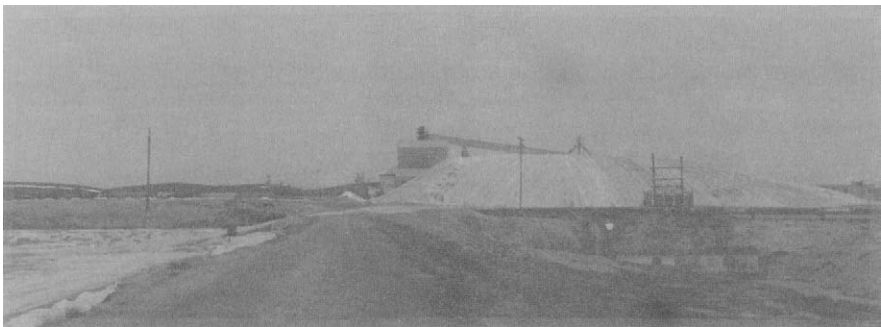


Figure 4.4 Saskatchewan Minerals Chaplin Lake facility. Cooling pond, left; brine inlet canal and pumps, right; glauber salt storage pile, center; plant, center rear. (Courtesy of Saskatchewan Minerals.)

dryer could be eliminated by recycling considerable dried product (a ratio of at least one, and preferably three parts of dry product to one of feed), but this required much more equipment (Miller, 1958; Holland, 1951, 1949).

As the production rate increased and became more competitive (thus requiring greater efficiency), and with tighter product specifications, five Holland evaporators (Fig. 4.5) replaced the rotary dehydrators, and the fuel was changed from lignite to Bunker C fuel oil, and later to clean-burning gas. The Holland units had the shape of a 3×4.3 by 3.7 m high ($10 \times 14 \times 12$ ft) stainless steel box and were fed $>60\%$ water content (entrained brine, the water from ice, and the water of hydration) crushed mirabilite. It entered a melting chamber containing a hot slurry, and as it melted two “beaters equipped with spiral paddles” rotating at 375–400 rpm throughout the vessel and with “cups between the spirals” splashed and threw the slurry into the upper section as a crude spray. Hot flue gas from both (or either) the salt cake dryers (at 260°C [500°F]) or from direct gas firing (at $816\text{--}982^{\circ}\text{C}$ [$1500\text{--}1800^{\circ}\text{F}$]) passed through this spray at a rate of 24,000 cfm (at Chaplin Lake all of the Holland units were fuel-fired, and three also received flue gas from the dryers). The water in the glauber salt was evaporated at a rate of 4.6 t/hr, and anhydrous sodium sulfate was crystallized. An expanded dome allowed much of the spray to settle before the vapors were vented at $71\text{--}82^{\circ}\text{C}$ ($160\text{--}180^{\circ}\text{F}$) and 80–95% humidity.

A drag chain or auger removed the solids from the base of the spray chamber, allowing them to partially drain to a 24–30% water content. The drained solids initially were sent directly to the dryers, but later they went to a filter to reduce the moisture content to 10%. The two dryers were conventional 2.1×18.3 m (7×60 ft) counterflow 316 stainless steel rotary units producing a hot (204°C), dry product

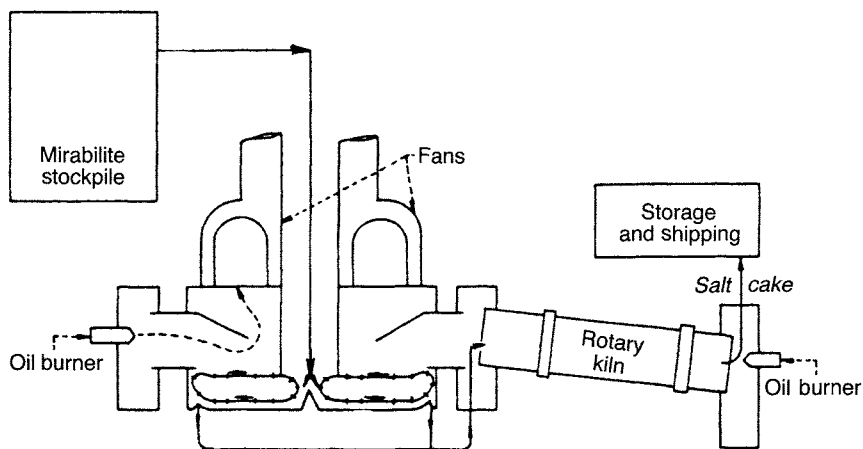


Figure 4.5 Holland evaporators (direct fired, left; heated by flue gas, right). (From Broughton, 1976, courtesy of the Montana Bureau of Mines and Geology.)

with a plant capacity of 400 t/day. After screening, the oversized product (+4.8 mm [3/16 in]) was ground in a 0.9×2.4 m rod mill, and the combined 98.5–99.5% Na_2SO_4 product stored in two 12×12 m silos (total capacity, 18,000 t; Miller, 1958; Holland, 1951, 1949). As an interesting by-product for the operation at Chaplin, about 45 t/yr of brine shrimp (*Artemia salina*) were harvested from the lake as a tropical fish food from 1968 to 1976 (Rueffel, 1976).

As the demands for production efficiency and product purity further increased, submerged combustion evaporators (Fig. 4.6) replaced some of the Holland units, and beginning in 1982 only a triple effect evaporator was utilized. At that time the process was also changed to produce a much higher-purity product. In 1999 glauber salt was reclaimed from the storage pile by an underneath drag conveyor, kept full by periodic loading (every 10–60 min) by a contract employee's bulldozer. The glauber salt was a greenish-brown color from the crystallizing pond's algae and brine shrimp population, and also contained some sand, clay, and rocks from the accidental harvest-contacting of the pond's bottom or sides, as well as windblown dust. From the drag conveyor it dropped onto a long inclined conveyor belt (Fig. 4.7) taking it under a tramp iron magnet and then to the plant. The flow rate was controlled

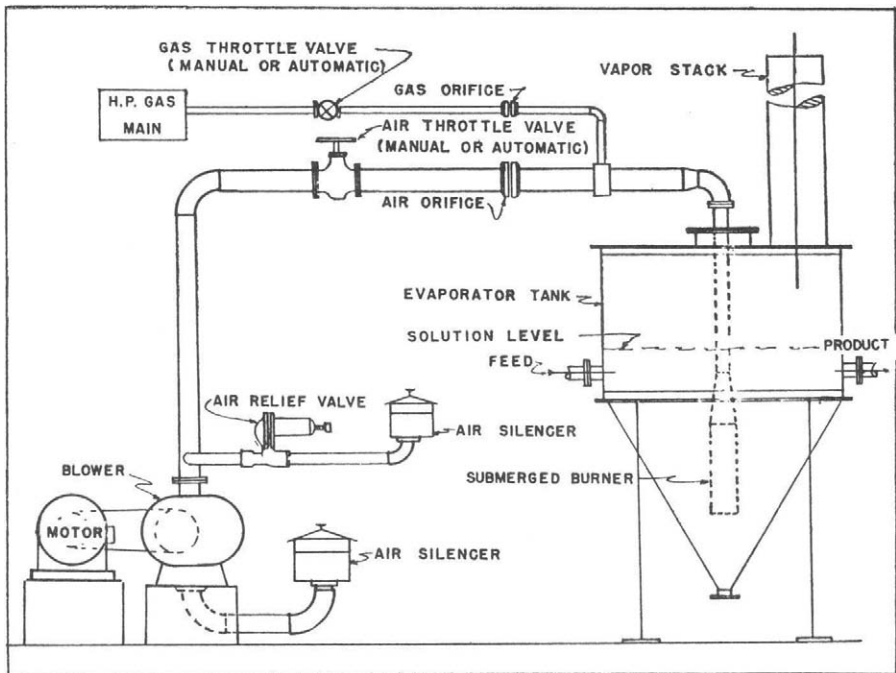


Figure 4.6 Typical submerged combustion evaporator installation. (From Weisman and Anderson, 1953, by permission of the AIME. First appeared in *Mining Engineering*, July 1953.)



Figure 4.7 Glauber salt conveyor belt at the Chaplin Lake plant. (Courtesy of Saskatchewan Minerals.)

(by start and stop operation) from the level controller in an agitated dissolving tank. In it the glauber salt was dissolved at about 40°C by second and third effect condensate from the evaporator, with the dissolver's water being flow-controlled by a density meter on the tank set at 30°Be (1.261 g/cm³; saturated at ~29°C). Rocks were occasionally removed from the base of the cone bottom on the dissolving tank,

but its brine pump still suffered considerable wear because some sand was present. Sleeves were used in the pipeline elbows from the dissolver and replaced at about 6-month intervals. The dissolved glauber salt brine then went to a settler-skimming tank where a coagulant (Percol 156 from Allied Colloids) was added to help in the skimming of much of the organic matter (primarily dark green algae, which was discarded) from the top of the tank. Sand also settled in its bottom cone and was withdrawn and thickened by a screw conveyor in an underneath inclined pipe. The brine was discharged from the center of the tank, and 100 cm³/min per 150 gpm brine flow of hydrogen peroxide were added as an organics removal agent in the next tank. From there the brine flowed to a 12.2 m (40 ft) diameter thickener with an 8-hr residence time to assist in the organics oxidation. The thickener's overflow was sent to the evaporator's feed tank, and its underflow joined the skimmer tank's screw conveyor to be periodically discarded.

Centrate from the product centrifuge joined the incoming feed brine in the feed (surge) tank and was distributed evenly to each of the evaporator's (Fig. 4.8) three effects. A slurry density of 30–34 vol% was maintained in each effect, and some

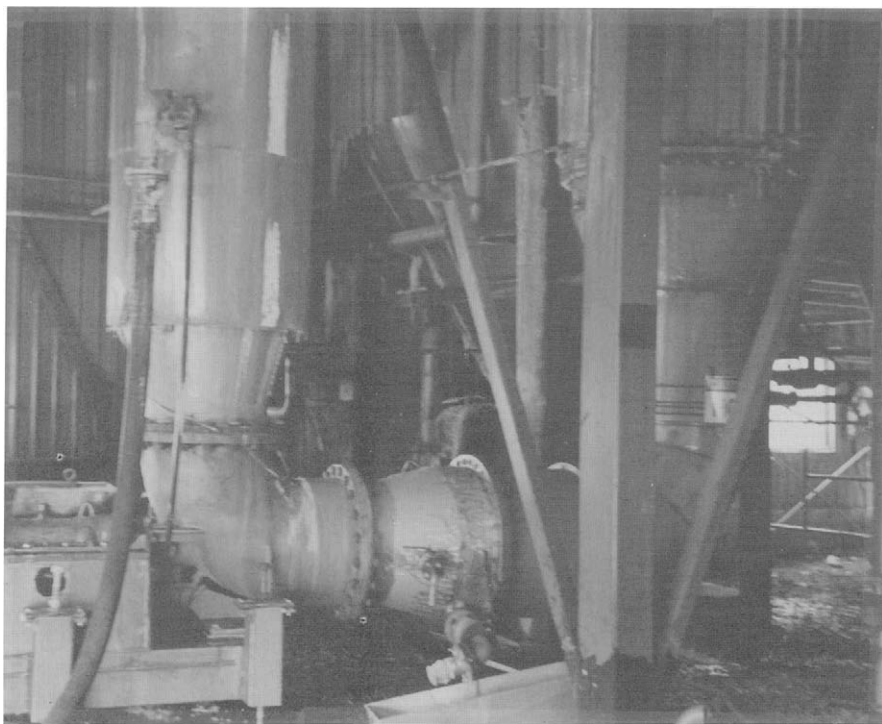


Figure 4.8 Sodium sulfate evaporators at the Chaplin Lake plant. Heat exchanger, left; circulating pump, center; evaporator, right. (Courtesy of Saskatchewan Minerals.)

slurry was also continuously withdrawn and sent to a screen bowl centrifuge. No defoamant was required in the evaporator bodies, only a very small bleed stream was taken from them, and first-effect condensate was returned to the two Cleaver Brooks boilers. The plant operated in 1999 with a cycle consisting of 10-day working period and 4 days off. During the down time the evaporator was washed. A dilute sulfamic acid solution was utilized (hydrochloric acid had been used) to help wash the titanium alloy tubes in the evaporator's heaters. The centrifuge had a capacity of up to 600 t/day (450 t/day was the average production rate) and discharged a cake with a 6–7% moisture content. The outer edge of the scroll in the centrifuge was built up with hard-facing welding rod once per year. There was no product washing on the centrifuge, but water was sprayed onto its screen, which partially dissolved some of the fines in the centrate.

The centrifuge cake was sent to a 2.1 m (7 ft) diameter, 30.5 m (100 ft) long gas-fired, cocurrent rotary dryer. It contained lifters only after the first 12 m (40 ft), and no external knockers. The small amount of fines carried over in the flue gas had a lower purity (96–97% Na_2SO_4) and so were discarded, redissolved, or sold separately. The product from the dryer was sent to a scalping screen, the oversize was crushed, and then the product was sent to storage silos with a 13,000 t capacity. From there it was shipped in 100-t rail cars, or by trucks. Unit trains were used for export shipments, and a series of warehouses in key cities allowed for very rapid bulk and bag delivery by truck to their customers. The company employed 80 full-time people (including administration) for their two plants (the other was at Ingebright Lake), with additional staff required in the summer for dredging at Ingebright, and contract workers needed for harvesting and some other jobs (Lavineway, 1999; Halbur, 1999; Jackle, 1999).

Horseshoe Lake (Horseshoe Lake Mining Company, 1930–1938)

The initial operation at Horseshoe Lake harvested mirabilite directly from its near-surface (there was 0.15–0.6 m of overburden and then up to 9 m of ore) and employed a very cumbersome dehydration process. The mirabilite (88.1% Na_2SO_4 , 9.6% insolubles, 2.3% other salts on a dry basis) was first reduced to a –2.5 cm (1 in) size in a roll crusher, and then washed (to 93.9% Na_2SO_4 , 4.5% insolubles, 1.6% other salts) in two 18-m long log washers. The fines were removed, and the ore was drained and then melted in two 9-m long, 1.4 m diameter rotary drum melters that were fired by lignite (with a 32.3% fuel efficiency). From there the slurry was pumped to 16.3-m long, 1.2-m diameter drum evaporator-dryers, where the slurry was sprayed onto the top of the outer, heated surface of the rotating drums, and scraped off at the bottom of the drums. The slurry was heated to its 103°C (218°F) boiling point by reject (8–10 psi) steam from a 300-kW turbine (the boilers had a 45% lignite fuel efficiency). The 27% moisture solids from the drum evaporators were transported by screw conveyors to two direct-fired (with lignite), 12-m long, 1.8-m diameter rotary dryers, discharging at 120–140°C. The plant operated for 6 months of each year with a capacity of 175 t/day of a 95.0% Na_2SO_4 , 4.1% insolubles, 0.9% other salts product (Pierce, 1938).

Horseshoe Lake (Ormiston Mining & Smelting Co.)

The second method of directly obtaining mirabilite from the sodium sulfate lakes in Canada was by conventional dredging, as practiced in later operations at Horseshoe Lake (Fig. 4.9), and by others at *Ingebrigt*, *Snakehole*, and *Sybouts lakes*. At Horseshoe Lake the slurry from the dredge working in the southern, high-purity end of the lake was initially sent to a washing plant, and the washed mirabilite was “melted” in its own water of hydration, leaving from 5 to 18% solid-phase

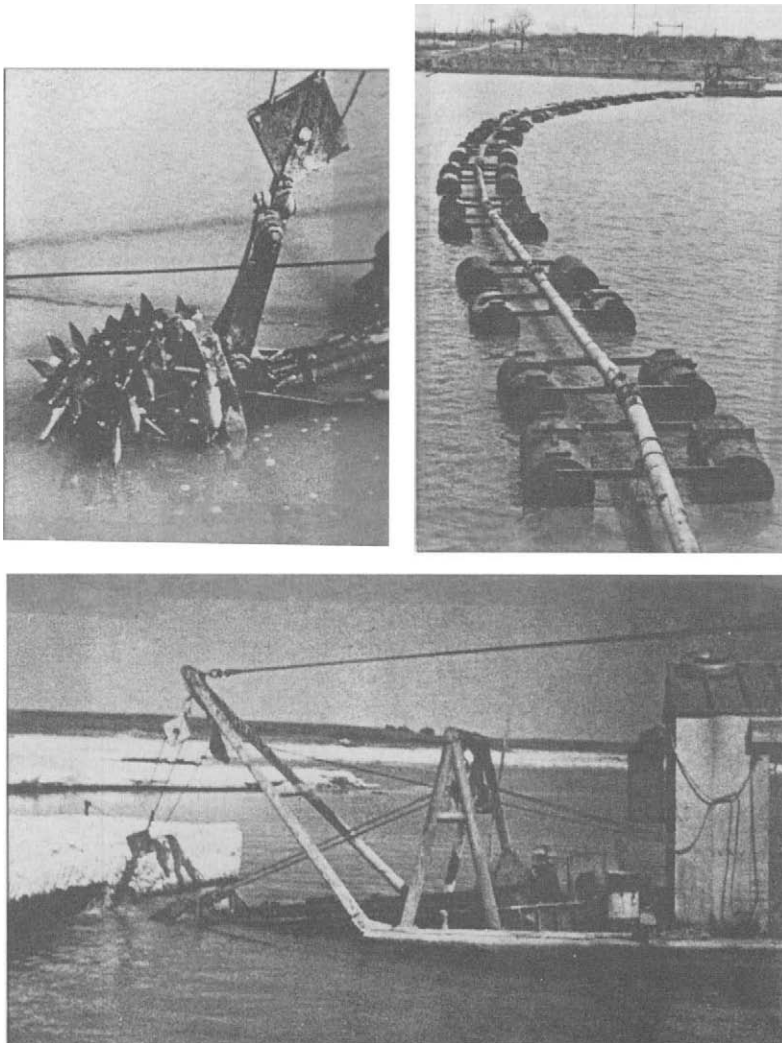


Figure 4.9 Floating mirabilite ore dredge. (From Rueffel, 1976, courtesy of the National Research Council of Canada.)

anhydrous sodium sulfate in the melted slurry. This slurry was then sent to a conventional triple effect evaporator, and from it a product slurry was removed, centrifuged, dried, and usually shipped in bulk 100-t hopper cars. Later, and at the other lakes, in order to obtain a purer product the dredged mirabilite was centrifuged, dissolved, and the resulting solution clarified before being recrystallized or sent to evaporators to form the anhydrous product (Rueffel, 1976, 1968). Ormiston Mining had the distinction among the Canadian sodium sulfate producers of attempting to produce sodium bicarbonate and ammonium sulfate from their ore by means of a modified Solvey process. They experimented with this process during the 1990s, including operating a pilot plant with a stated 75 t/day sodium bicarbonate capacity. The operation was never commercialized, however, and even though modernizations to make a detergent-grade sodium sulfate had been announced, the company's Horseshoe Lake plant was closed in 1998 (Anon., 1998).

Ingebright Lake (Saskatchewan Minerals)

For lakes with extensive bedded mirabilite, but some to considerable mud interlayering, various methods of recovering mirabilite have been attempted. Ingebright Lake initially was mined by both earth-moving equipment (in the higher-grade southern part of the lake during the summer) and a surface solution mining method. For the latter operation an adjacent freshwater reservoir was first constructed to hold runoff water as well as water pumped at 500 gpm from three wells. This water was then flooded onto another portion of the southern area of the lake surface in the summer to maintain about a 15-cm depth, and a "tracked swamp vehicle" was driven through the brine to help mix it. As the brine reached saturation it was pumped at 2000 gpm into holding ponds near the plant to crystallize mirabilite in the autumn. The residual brine was sent to separate impoundments or returned to the lake, and the mirabilite was windrowed in order to drain, harvested in the late fall, and sent to a stockpile. In the plant the mirabilite was dehydrated and sold as a medium-purity product (Rueffel, 1968).

Later an improved solution mining system was used to obtain the ore, along with dredging (the dredged product was dissolved and added to the solution mining brine). For the solution mining, 30 holes 6 m apart were drilled to the base of the mirabilite (up to 30.5 m [100 ft] deep; Jackle, 1999), and 3.8-cm pipes were placed in them. Brine was heated to 49°C (120°F) and then injected into the holes, to be forced through the mirabilite bed and returned to the lake's surface, where it settled. Some was recirculated, and eventually, when nearly saturated, it was pumped to holding ponds to be crystallized in the fall. This system was abandoned in the late 1960s, and dredging alone with a 12-m depth capability replaced it (Fig. 4.9). The dredges operated in 1999 from April–May to October–November on a 24-hr, 7 days/wk schedule, and the recovered mirabilite was filtered and either stockpiled or sent directly to the plant (Lavineway, 1999).

In the early days of plant operation the directly harvested and crushed ore was first sent to six Holland evaporators for the mirabilite dehydration (Broughton, 1976), but in their later 600 t/day plant (Fig. 4.10) a submerged combustion melter and two lines of submerged combustion evaporators were employed. A slurry of anhydrous

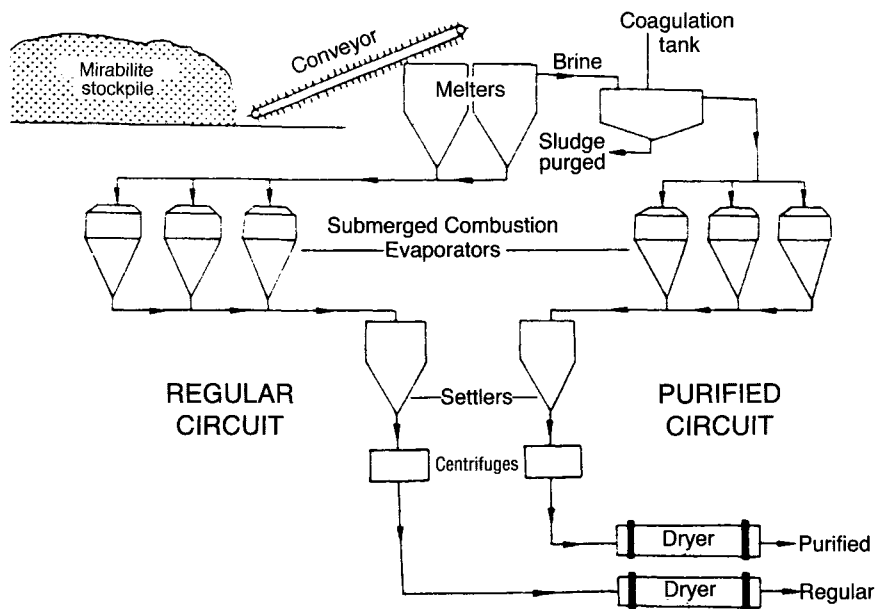
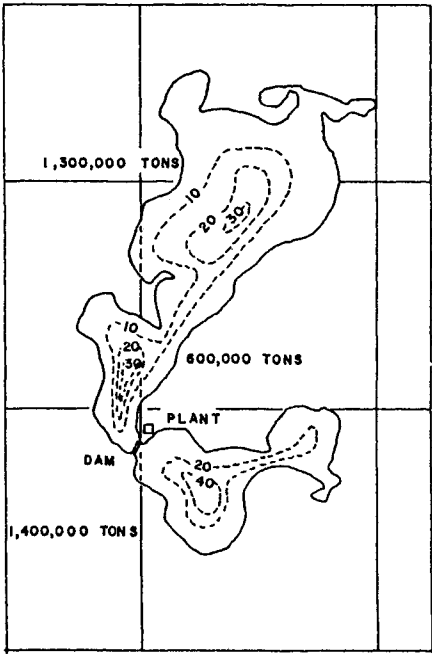


Figure 4.10 Flow diagram of the Ingebright Lake plant in 1976. (From Broughton, 1976, courtesy of the Montana Bureau of Mines and Geology.)

sodium sulfate was continuously removed from the evaporators, thickened, and then sent to a screen bowl centrifuge. This reduced its moisture content to 6–8%, and the centrate and thickener overflow were returned to the evaporator. The cake was next dried in either of two 304 stainless steel-clad rotary, parallel flow dryers, leaving at 168°C. This produced a whiter, easier to handle, less-caking and dusty product, which was stored in silos with a capacity of 11,000 t (Rueffel, 1968).

Metiskow Lake (Alberta Sulfate Limited)

A much improved solution mining technique was later developed for the high-insolubles, high-carbonate mirabilite at Metiskow Lake. A dilute brine was first heated in the plant to greater than 38°C (100°F) by being sprayed into the top of a tower with rising flue gas from the boilers and dryers. The warm brine was then injected into the salt formation through a series of pipes that extended to the base of the mirabilite bed (Fig. 4.11). The brine dissolved (and melted) the mirabilite, and the mud and insolubles settled out (without, one would hope, burying too much of the mirabilite). The pipes had been rather easily inserted into the formation by the warm brine dissolving or blowing away material to form their holes. As the injection brine accumulated it created a large pool around the pipes that was nearly 38°C at its base, and even in the winter (with a solid ice cover) was 27°C (80°F) 1.2 m below the surface. The total salt (mainly Na_2SO_4) concentration of the brine was maintained at 20–30%, and at a concentration that would only be saturated at 2.8–5.6°C (5–10°F)



Metiskow Lake

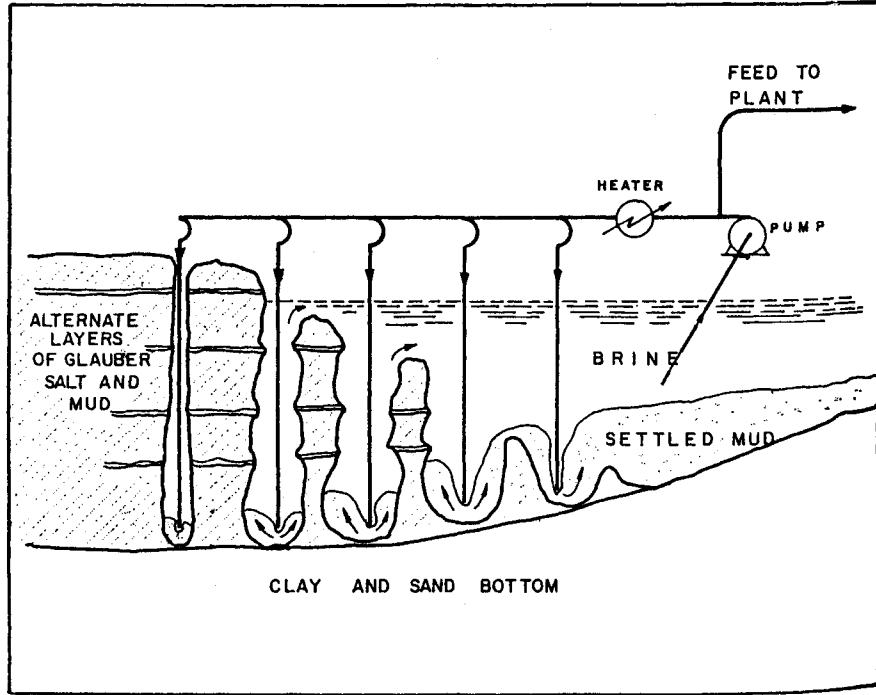


Figure 4.11 Solution mining at Metiskow Lake, Alberta. (From MacWilliams and Reynolds, 1973. Figure published in *CIM Bulletin*, Volume 66, Number 734. Reprinted with permission of the Canadian Institute of Mining, Metallurgy, and Petroleum.)

below the brine's actual temperature (so as not to crystallize in the pipes). A stream of brine from the pool was constantly withdrawn and recirculated through the heaters to keep it warm and at the desired concentration, and some of this brine was retained in the plant for processing. There it was first sprayed into the top of a modified cooling tower that acted as an air-cooled crystallizer, and a mirabilite slurry was removed from its base and thickened. The cooled overflow brine was returned to the heater and then the lake, with a large bleed stream removed to prevent the buildup of sodium carbonate and other salts. The solution mining holes were frequently taken out of service and new ones added when it was determined that the optimum amount of mirabilite from the old area had been recovered.

The mirabilite slurry from the coolers was next thickened, centrifuged, and washed, with the overflow brine and centrate being returned to the heaters. The mirabilite cake was then conveyed to a submerged combustion evaporator where its water of hydration was removed and anhydrous sodium sulfate crystallized. The resulting slurry was again thickened and centrifuged, with most of the brine and centrate returned to the evaporator. A bleed stream was again removed to control the level of impurities. The product was next dried in a rotary dryer, screened, and sent to storage (MacWilliams and Reynolds, 1973).

Other Canadian Operations

In 1934 an operation on *Whiteshore Lake* (*Midwest Chemicals Limited*) harvested mirabilite directly, but they later (and continuing into 1999 as *Millar Western*) generated their mirabilite in holding ponds during the autumn (Fig. 4.1). Submerged combustion evaporators were used in the plant. At *Sybouts Lake, East* (*Sybouts Sodium Sulfate Company Limited*) there was an operation from 1941 to 1983 that produced 850,000 mt of product. It initially generated mirabilite in the fall from brine in a clean depression on the lake, or in ponds. It was processed by two 1.8-m diameter, 33.5-m long dehydrator-dryers, and later they employed submerged combustion evaporators (Rueffel, 1976; Tomkins, 1954). The later operation at *Alsask Lake* (*SOTEC Company*) was reported to have built a glaserite ($\text{Na}_2\text{SO}_4 \cdot 3\text{K}_2\text{SO}_4$)-based potassium sulfate plant using their own sodium sulfate as a raw material (with purchased potash [KCl]), but the company went bankrupt in 1997 before any production had been obtained. In 1999 this plant was still in the hands of the receiver, although the equipment for their sodium sulfate production had been sold (Lavineway, 1999). In 1999 the only Canadian sodium sulfate lakes still in operation were Saskatchewan Mineral's two plants at Chaplin and Ingebright Lakes, and Millar Western's Whiteshore Lake near Palo or Begger, Saskatchewan. Also, *Big Quill Chemicals* at *Big Quill Lake* produced potassium sulfate from sodium sulfate by an expensive ion exchange process (with a reported 10,000 t/yr capacity). However, they purchased both of their raw materials (potash and salt cake), even though the lake had large sodium sulfate reserves (primarily as brine). Plans to construct a 50,000 t/yr glaserite-based plant were announced in 1998 (Anon., 1998; Husband *et al.*, 1966; Miller, 1958; Edmunds, 1957; and Cole, 1926). Table 4.1 lists the lake and operating period for various of the Canadian sodium sulfate producers.

Table 4.1
Some Companies That Have Produced Sodium Sulfate in Canada^a

Years	Company	Lake
1918–1919	Canadian Salt and Potash Co. of Canada Ltd.	Muskiki
1919–1923	Salts and Chemicals Ltd.	
1934–1938	Muskiki Sulfates Ltd.	
1920–1923	Soda Deposits Ltd.	Fusilier North
1927–1931	The Sodium Sulfate Refining Co.	
1931–1938	Dominion Sodium Refineries	
1921–1955	Bishopric and Lent Co. Natural Sodium Products	Frederick
1955–1983	Saskatchewan Minerals	
1921–1925	Soda Lake Chemical Co.	Alsask
1926–1941	Sodium Corporation Ltd.	
1941–1954	Natural Sodium Products	
1954–1969	Sodium Sulfate Co. of Saskatchewan	
1969–1991	Francana Minerals (Agassiz Resources)	
1993–1997	Salt of the Earth (Sotec)	
1930–1950	Horseshoe Lake Mining Co.	Horseshoe
1950–1969	Midwest Chemicals Ltd.	
1969–1998	Ormiston Mining and Smelting Co.	
1931–1933	Canadian Salines Ltd.	Whiteshore
1934–1980	Midwest Chemicals Ltd.	
1980–present	Millar Western	
1932	G.M. Lyons	Sybouts East
1941–1983	Sybouts Sodium Sulfate Co.	
1932–1933	Metallics and Non-Metallics	Ingebright South
1967–present	Saskatchewan Minerals	
1933–1934	Fred Solomon	Regina Beach South
1935–1937	Oban Salt Co. Ltd.	Oban
1935–1954	Sodium Sulfate Co. of Saskatchewan	Ceylon
1947–present	Saskatchewan Minerals	Chaplin
1952–1967	Saskatchewan Minerals	Snakehole
1967–1991	Francana Minerals (Agassiz Resources)	
1993–1997	Salt of the Earth (Sotec)	
(?)	Midwest Chemicals Ltd.	Metiskow (Alberta)
(?)–1978(?)	Alberta Sulfate Co.	
1978–1991	Francana Minerals (Agassiz Resources)	
1993–1997	Salt of the Earth (Sotec)	

^a Adapted from Tomkins, 1954.

Chile

Soquimich (Sociedad Quimica y Minera de Chile)

The complex Chilean nitrate ore contains sodium nitrate, sodium sulfate, and sodium chloride as its major components, with each varying independently, usually in the 6–10% range, but the sodium sulfate is sometimes up to 15%. The most valuable components are sodium nitrate (with a smaller amount of potassium nitrate) and iodine, whereas sodium sulfate and boric acid have a secondary value. However, because of the very large amount of sodium sulfate present, it has also become a major product (160,000 mt/yr of capacity has been announced; Anon., 1998). There are two plants producing this material, with different processes for leaching the ore and recovering the sodium nitrate, which somewhat changes the processing possibilities for the sodium sulfate.

At the Maria Elena plant (built in 1927) the coarse ore is leached in 10 large vats operated with the leach liquor advancing from vat to vat in a flow that is counter-current to the freshness of the ore. The leaching is done by circulating the liquid 8–14 hr in each vat in an upward flow at 40°C until it reaches the desired concentration, and then it is drained and advanced to the vat with the next less-depleted ore. When the concentration reaches about 440 g/liter of NaNO_3 , the liquor is removed, cooled to 5°C to crystallize sodium nitrate, and then sent to the iodine plant. If only the residual liquor from this plant were returned to the leach vats, the leaching could be made totally selective for sodium nitrate and iodine, since the brine would always remain saturated with the other salts, and thus not dissolve them. However, the small amount of make-up water equal to that lost in the system would not allow a very efficient washing of the residual ore, and the unleached ore and entrainment losses would be considerable.

Consequently, solar ponds were constructed in 1951 to evaporate additional water, thus allowing more to be used in washing the leached ore. When the nitrate in the ore of the next-to-last vat had been depleted to an economic minimum (1.5–2% NaNO_3) the vat was drained, and later as the last vat washed with this additional water, reducing its nitrate content to 0.3–0.5% NaNO_3 . The wash water was then used for leaching the fine ore that had been screened and was not sent to the vats. It next leached the next-to-last vat, and after being cooled to crystallize glauber salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) the residual brine was sent to solar ponds. There were initially 10 of these ponds, each 200×220 m in size and operated with a liquid depth of 50 cm. A mixture of primarily sodium chloride and astrakanite ($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$; 5 t/t NaNO_3) was deposited in them as an average of 2400 m³/day of water evaporated, and the salts were periodically harvested for later use in the sodium sulfate plant, or to be discarded. The concentrated brine from the ponds could then be cooled to different temperatures to produce any or all of pure sodium nitrate, a potassium–sodium nitrate mixture, or (with the addition of potassium chloride) as much potassium nitrate as desired (Fig. 4.12). Some of the residual brine joined the main brine stream at the iodine plant, and the rest was returned to the solar ponds to evaporate further.

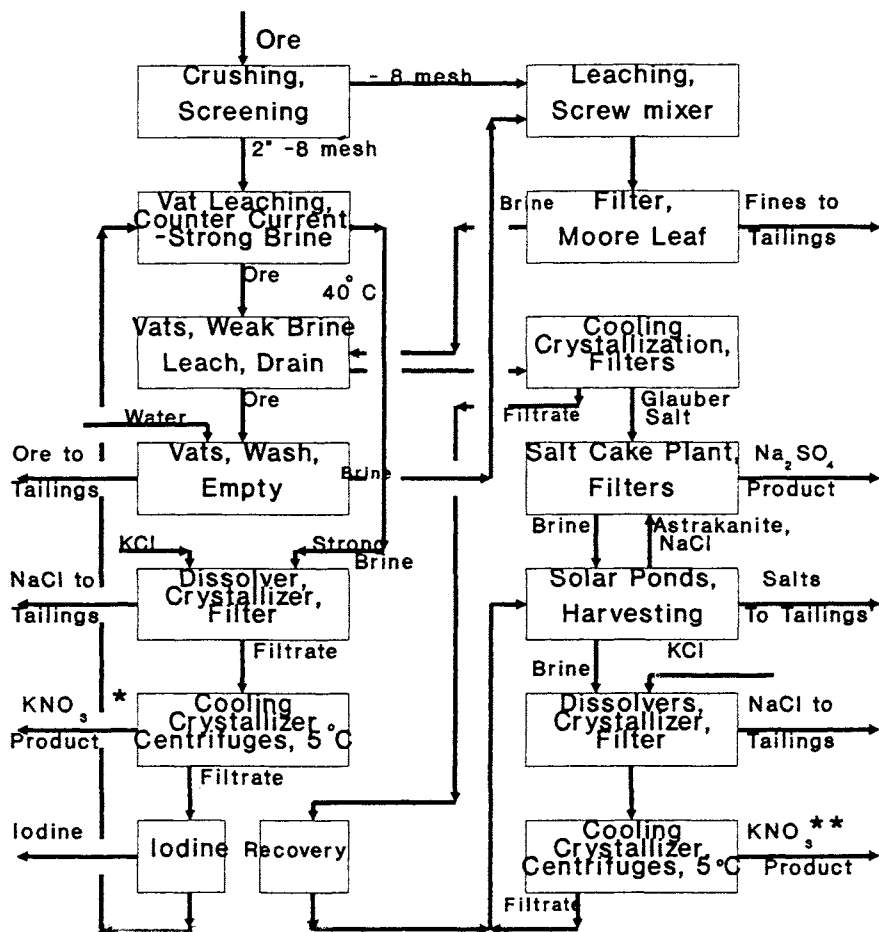


Figure 4.12 Flow sheet for the Maria Elena nitrate-iodine-sodium sulfate plants. (*) Without KCl addition, pure NaNO_3 is produced. (**), Without KCl addition a mixed NaNO_3 - KNO_3 product is made. From Garrett (1996); with permission of Kluwer Academic Publishers.

The fine ore (-8 mesh; about 15% of the total), as noted above, was leached in a screw mixer at 100°C with the weak brine from the water-washing of the drained final vat, and then filtered and the filter cake discarded. The filtrate left as a dilute solution of all of the salts in the ore, and was sent to the next-to-last leaching vat to be leached again. It was circulated through the vat, dissolving additional sodium nitrate and becoming saturated with most of the other nonnitrate salts (primarily sodium sulfate and sodium chloride). This brine was next cooled to crystallize glauber salt, which was thickened from the cooled solution, filtered, washed, and sent for further processing. Some of the residual brine next went to the iodine plant,

and the other was returned to the solar ponds. Glauber salt could be recovered from the next-to-last vat's brine in amounts up to a fairly high percentage of the ore's total sodium sulfate content, depending on the temperature to which the brine was cooled and the amount of water washing in the final vat.

Solar Pond Dehydration

The nitrate–iodine cycles described previously thus provided glauber salt and an astrakanite–sodium chloride mixture as potential raw materials for a sodium sulfate plant. The possible processing methods for glauber salt were well known, and the initial moderately large-scale salt cake production from 1967 to 1978 was by dehydrating the glauber salt in solar ponds. The glauber salt was pumped to clean ponds in a sodium chloride solution and heated by flue gas from the power plant to maintain a temperature above 19°C. This allowed anhydrous sodium sulfate to crystallize in the ponds, and it was periodically harvested, washed, dried, and sold as a medium-purity product. It contained a small amount of insolubles from wind-blown dust that settled in the ponds, and some sodium chloride and other impurities. Its particle size covered a wide range, partly because some mirabilite also crystallized, and it formed a fine powder when dehydrated in the dryer. As the demand increased for greater production and a purer, more closely sized product, a new process was required.

Sodium Sulfate from Astrakanite

Each of the studies to this end were involved with methods of utilizing the astrakanite, and initially a flotation process was developed to make a crude separation of the astrakanite from its accompanying sodium chloride. After the salts were harvested and ground to a small particle size much of the astrakanite could be floated when using a sodium naphthanate reagent. The very small liberation size was a problem, but still a partial separation could be made with much of the sodium chloride rejected in the underflow. The concentrated astrakanite was then reacted at 95°C with a solution just saturated with sodium chloride to convert the astrakanite into solid-phase vanthoffite ($3\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4$) and magnesium chloride that remained in solution. The vanthoffite was filtered and washed, and then leached at 55°C with a sodium chloride solution to dissolve its magnesium sulfate content, leaving behind (actually recrystallizing) much of the sodium sulfate. There was also some reaction of magnesium sulfate with the sodium chloride to produce more sodium sulfate (and magnesium chloride in solution), but this reaction was very slow and incomplete. This ingenious process was not commercialized, however, because the yields were quite poor, the vanthoffite conversion was slow and variable, and many of the solid impurities in the harvested salts remained with the product (Galleguillos and Gonzalez, 1983).

Salting-Out Process

The process that was adopted in 1979 and used to the present time involves the salting-out of anhydrous sodium sulfate from glauber salt by means of the

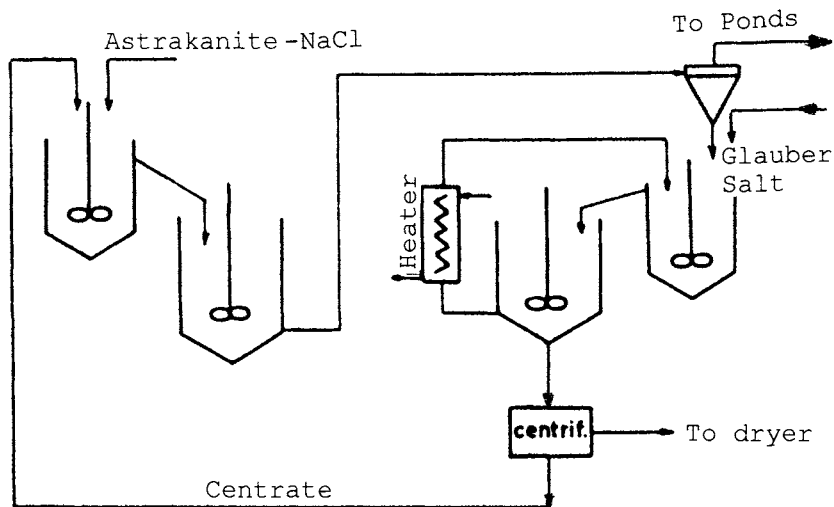


Figure 4.13 Flow sheet for the Soquimich salting-out sodium sulfate plant. (From Galleguillos and Gonzales, 1983, courtesy of *Minerales*.)

astrakanite-sodium chloride mixture obtained from the solar ponds. In this manner some of the sodium sulfate in the astrakanite is recovered as a product, and a fairly pure product is obtained. This is accomplished by conducting the salting-out in two countercurrent stages, and operating the stage where glauber salt is added at less than sodium chloride and magnesium sulfate saturation (Fig. 4.13). An analysis of the raw materials for the process is shown in Table 4.2, indicating the range of compositions that are usually obtained for the astrakanite-salt mixture. In the process crushed astrakanite-salt is added to the first of two agitated tanks in series containing

Table 4.2

Raw Material and Product Analyses for the Soquimich Salting-Out Sodium Sulfate Process (wt%)^a

	Glauber salt	NaCl in Astrakanite-NaCl Mixture			Product
		High	Medium	Low	
Na ₂ SO ₄	40.0	13.2	15.5	18.7	99.00
NaCl	1.04	57	51.3	43.7	0.50
MgSO ₄	0.3	12.6	14.9	17.8	0.15
H ₂ O	58.66	15.6	16.9	18.7	—
Insolubles	—	—	—	—	0.008
Reflectance	—	—	—	—	88.0

^aGalleguillos and Gonzalez, 1983

a brine that is saturated with sodium sulfate but not salt or magnesium sulfate. This allows some of these salts to dissolve, and the proportionate amount of sodium sulfate to precipitate. There is also a very small amount of reaction between the sodium chloride and magnesium sulfate, precipitating more sodium sulfate. The slurry that is formed is then sent to a settling cone where the salts settle, and most of the solution and the fines (including some of the insolubles in the harvested salts) pass out the top and are rejected.

The astrakanite–sodium chloride–sodium sulfate mixture is then added with the glauber salt into a two-stage reactor held at a temperature of 40°C. The glauber salt is dehydrated at that temperature (providing all of the water for the process) and salted out by the presence of the other salts (it actually dissolves, and the anhydrous sodium sulfate reprecipitates). The water that is liberated dissolves all of the salt and the magnesium sulfate in the astrakanite, precipitating more sodium sulfate and providing the salting-out effect. A deficiency of the mixed salts is added in order to ensure that none leaves with the product, and thus sodium chloride and magnesium sulfate saturation is not obtained. A typical product analysis is shown in Table 4.2, although the low insolubles that are indicated would appear to be a minimum, since most of the insolubles in the harvest salts should follow through into the product. The initial plant capacity was 60,000 mt/yr, and some of the product was said to be sold to high-quality markets such as detergents and cosmetics (Galleguillos and Gonzalez, 1983). In 1998 an additional 100,000 mt of sodium sulfate capacity were announced (Anon., 1998), presumably from the Pedro de Valdivia plant by cooling a wash water to form glauber salt and dehydrating it in multiple effect plant evaporators to produce a higher quality product.

Mexico

Quimica del Rey

The world's largest production of sodium sulfate in 1999 was obtained by Quimica del Rey, S. A. de C. V., a wholly owned subsidiary of Industrias Penoles, S. A. de C.V. Their first plant began production in 1964 with a capacity of 50,000 mt/yr of high-quality Na_2SO_4 , was expanded to 60,000 t/yr during startup, and in 1999 had a capacity of 620,000 mt/yr. Brine at 25°C was initially obtained from the Laguna del Rey by 65 wells about 12 m deep in the northeast corner of the playa. To crystallize glauber salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), the brine was first heat-exchanged with cold end liquor, and then further cooled in vacuum crystallizers to 13°C. The glauber salt was removed from the crystallizers, thickened, centrifuged, washed, and “melted” by steam from the evaporator's third effect. The resulting slurry was then sent to a triple effect evaporator, and a sodium sulfate slurry continuously removed. It was thickened, centrifuged, washed, and dried in a cocurrent, oil-fired rotary dryer. The spent brine from the glauber salt crystallizers and centrifuge was heat exchanged with the entering brine and sent to holding ponds at the north end of the lake. Here it evaporated and deposited astrakanite

($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$), which was gathered into large piles that were still present in 1999.

As a series of expansions occurred at Laguna del Rey extensive effort was expended to make the operation more efficient, require less utilities and fewer personnel, and produce a better product. This effort has been very effective, and the plant in 1999 was one of the most modern in the industry. A computer-assisted optimization program had been made for the recovery of brine from the lake, and as a result a series of injection wells for a mixture of water and spent brine were drilled in the north end of the deposit. Monitoring wells 5 cm (2 in) in diameter were also placed throughout the lake and sampled once per month to check the brine level and ensure that a uniform strong brine was entering the pumping wells with the minimum of drawdown and short-circuiting (of weaker brine). The injection wells have helped in maintaining the brine level in the playa, and assisted in more slowly and completely dissolving the salts from the periphery of the lake toward the center.

The total number of wells in the deposit in 1999 was about 250, with only 70–80 needed to supply brine for the plant. The pumping wells were 24–25 m deep with gravel packing in the bottom 12 m of open hole, and casing and a 5-HP submersible pump with its PVC piping located above that. The well pumps were manifolded to a 30.5-cm (12-in) PVC pipe, buried at a 1-m depth to keep the brine at its 25°C lake temperature and deliver the sparkling clear brine approximately 3 km to the plant. There were two small (~5000 gal) surge tanks and a pump along the line, and two larger receiving tanks at the plant. The deposit had about a 15% porosity in the pumping zone, and in 1999 the average brine had about a 200 g/liter sulfate content with a density of 1.3 g/cm³ and a pH of ~7. The average depth to the brine in the lake was about 8 m. The pump life was about 5 yr before repairs were required, and the well life averaged more than 15 yr. Fresh water was obtained from an aquifer on the other side of a major fault line about 4 km to the south of the plant. Its mineral content was ~3500 ppm (including 800 ppm Ca), and it was used directly in the plant and town for sanitary and other nondemanding purposes. Some was also softened, and after processing through a reverse osmosis installation was demineralized for drinking water and other higher-purity requirements (Guzman Paz, 1999; Reyes Rodriguez, 1999; Delgado Lopez, 1999).

In 1999, 6800 liter/min (1800 gpm) of brine was typically pumped from the storage tanks to the plant (Fig. 4.14). It was first cooled from 25°C to 21°C (just above its crystallization point) in a plate and frame heat exchanger by all or a portion of the cool reject sodium-sulfate-depleted brine (this was its final and third stage of utilizing its cooling ability). The feed brine then went in series flow to the first of seven evaporative-cooling (under increasing vacuum) glauber salt crystallizers (Fig. 4.15). The first crystallizer was cooled to 18°C by reject brine flowing through its barometric condenser (the second stage of utilizing cool reject brine), and the next five were cooled by cooling-tower water in barometric condensers with successively higher stages of vacuum created by steam jet ejectors. The seventh crystallizer was cooled by reject brine flowing through its barometric condenser, assisted



Figure 4.14 The Laguna del Rey sodium sulfate–Magnesia–Epsomite Plant. (From Penoles, 1997, courtesy of Servicios Industrias Penoles, S.A. de C.V.)

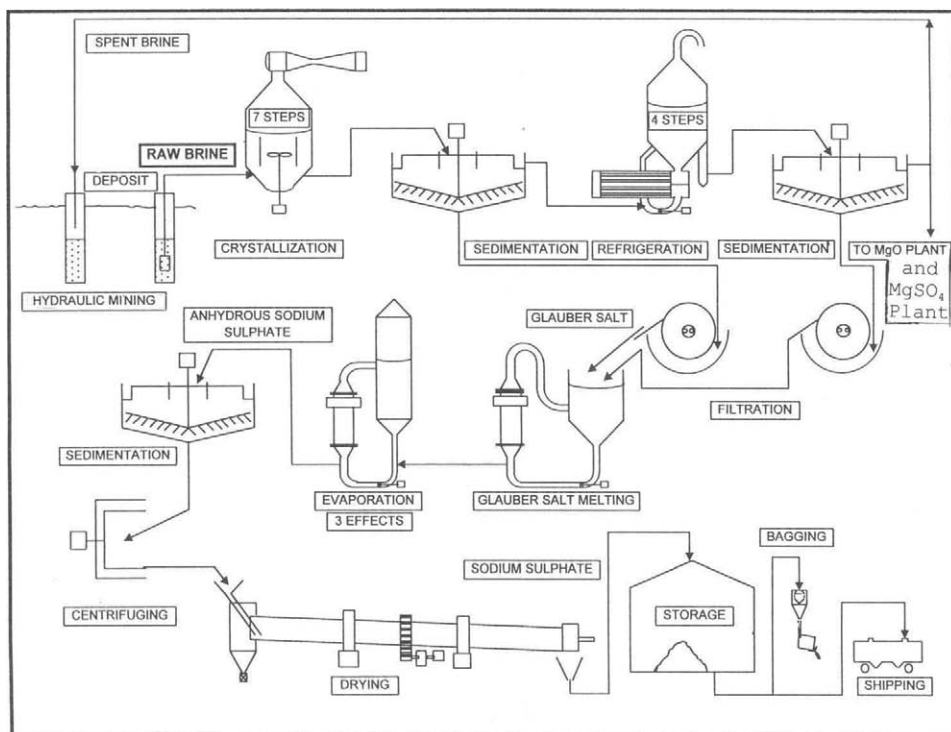


Figure 4.15 Flow sheet for the Laguna del Rey sodium sulfate plant. (From Ross, 1999, courtesy of Servicios Industrias Penoles, S.A. de C.V.)

by high-vacuum jets (the first stage of reject brine cooling). The glauber salt slurry from the seven crystallizers was sent to two thickeners, and the underflow was filtered in vacuum drum filters.

The thickener overflow streams and filtrate were next sent to four ammonia-cooled crystallizers (in series; Fig. 4.16) for the final stage of cooling. In each crystallizer a glauber salt slurry was circulated at a high flow rate through large shell and tube heat exchangers cooled to as low as -3°C by the vaporization of liquid ammonia. The ammonia vapor from these exchangers was then recompressed, cooled, and liquefied in plate and frame exchangers for another cycle of brine cooling. The glauber salt slurry from the final crystallizer was thickened and filtered, and the overflow and filtrate (the reject brine, or end liquor) with about 100 g/liter sulfate content was sent to the seventh vacuum crystallizer stage's barometric condenser. As the reject, heat-exchanged brine finally left the sodium sulfate plant, its volume was about 80% of the entering feed, and it was split into three equal parts: One was blended with fresh water and sent to the lake's injection wells, one went to the magnesium sulfate plant, and the final third was sent to the magnesium oxide plant.



Figure 4.16 Ammonia-cooled heat exchangers and crystallizers at Laguna del Rey. (From Penoles, 1997, courtesy of Servicios Industrias Penoles, S.A. de C.V.)

The glauber salt from the filters was melted at 50–70°C by vapor from the third effects of the plant's four sets of triple effect evaporators. The melted slurry was then fed into the third effects to be evaporated and crystallize anhydrous sodium sulfate. No bleed was taken from the evaporator circuit, and their condensate was returned to the boilers. Product slurry was withdrawn from each effect, thickened to ~80 vol%, and then centrifuged in 45 t/hr three-stage pusher centrifuges (the world's largest, built especially for this plant). No wash water was employed on the centrifuges, and the cakes' typical moisture content was 4%. From there the cake was fed to a long rotary dryer, fired by gas in countercurrent flow. The product was finally sent to storage (19,000 mt) for shipment by rail in bulk hopper cars, or about 10% was shipped in bags or bulk bags. Export shipments to Europe or South America were routed through the port at Tampico, whereas shipments to the Pacific Rim went through Manzanillo. In 1999 the plant worked three shifts, 365 days per year, had

a total of 14 MW of installed power, and purchased about 25% of its electricity needs from the country's power grid. Fuel for the plant was supplied by a 20-cm (8-in) gas pipeline (Ross, 1999; Reyes Rodriguez, 1999; Delgado Lopez, 1999).

Sulfate de Viesca

Near Viesca in northeast Coahuila, this plant has produced an estimated 22,000 mt/yr of sodium sulfate as a by-product from a salt operation (McIlveen and Cheek, 1994). The sodium sulfate plant was closed in 1999 (Ross, 1999).

Spain

Minera de Santa Marta

Minera de Santa Marta (MSM) is the youngest of the Spanish sodium sulfate producers, operating in the Rio Tiron–Belorado subbasin of Spain's northern Ebro Basin. The deposit is in the western corner of the Ebro Basin, near Burgos, and fairly near the shipping port of Bilbao. The initial plant was started in September of 1989, purchased by the SAMCA Group in 1995, and enlarged to 200,000 t/yr by the addition of a second parallel production line in 1997. The glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$) ore used by MSM is very pure, and the beds are flat (a maximum slope of $1\text{--}2^\circ$) and free from faults. However, the deposit consists of six major zones that contain some interbeds of shale and gypsum, and there are thicker layers of barren rock between the glauberite zones. For example, the average of one set of four drill holes (in their Cerezo formation) indicated that the six glauberite zones totaled 39.6 m in thickness, or an average of 6.6 m/zone (a range of 4.0–11.1 m). Each glauberite zone averaged one interbed (0–3) of barren rock, making 5.4 m of pure glauberite (2.4–9.2 m) and 1.2 m (0–2.4 m) of interbedded barren rock. The thickness of the barren rock between the glauberite zones averaged 3.1 m (2.0–4.3 m). The total ore reserves were 670 million t of glauberite averaging 33.5% Na_2SO_4 , or 225 million t of sodium sulfate. The exploitable reserves based upon the 1999 economy were 162 million t of 35% Na_2SO_4 glauberite, or 57 million t of Na_2SO_4 .

A unique mining plan has been developed to match the deposit's individual stratigraphy, consisting of first removing and storing the top soil, and sending the 5–15 m of overburden from a proposed leaching pit to the tailings pile. Then the ore from the first two glauberite zones is selectively mined and stockpiled, with the barren rock between the glauberite zones sent directly to the tailings area. Finally, the ore in the third glauberite zone is blasted in place to the desired rock size and interrock porosity. Blasting for all of the rock is done with ANFO and some dynamite by first detonating a row of holes around the edges of the pit to form a fairly smooth wall, and then blasting the remainder of the rock. Once the bottom ore zone has been fragmented, the previously mined ore is placed on top of it. The pit size is nominally 200×150 m, the average ore thickness 20–21 m, the bed's porosity 25%, and the rock size less than 400 mm. In 1999 the maximum distance from the pits to the plant was 2 km, and two 200,000 m³ plastic-lined water reservoirs



Figure 4.17 The Minera de Santa Marta (MSM) sodium sulfate operation. Leaching Pits, center left; tailings, upper left; temporary ore holding, lower left; water reservoirs, center right; plant, center, further right; Crimidesa, top center. (From MSM, 1997, courtesy of Minera de Santa Marta.)

were between the plant and the pits (the reservoirs were about 600 m from the plant; see Fig. 4.17).

Brine (or water) injection and withdrawal wells were then constructed 5–30 m apart on opposite sides of the 200-m dimension of the pit, with gravel packing somewhat similar to that of water wells. The injection wells discharged weak brine (or water) 3–4 m from the surface, and the withdrawal wells removed a nearly saturated brine from the bottom of the pit (Fig. 4.18). The piping manifolds had valves on each well so that the brine concentration could be controlled by the flow rate. This was monitored by checking the temperature (the leaching reaction is exothermic) and density of the exit brine each day, with chemical analyses once per month. The brine level in the ponds was kept 1–2 m below the surface to provide insulation, and rainwater generally adequately leached the overlying ore. After being completed a new pit would be filled with water, and the leaching process would commence.



Figure 4.18 The Minera de Santa Marta (MSM) initial glauberite leaching pits. (From Regueiro *et al.*, 1997.)

When the leaching of the upper three ore zones was completed, the spent ore would be removed and stockpiled to be later returned to a pit. The remaining three ore zones would next be mined and prepared in the same manner as the upper three, and then leached. When they were depleted the spent ore from the upper zone would be returned, the pit filled with the overburden from a new pit, and topsoil placed over that to return the mined area to its original or an improved condition.

By 1999 six pits were in operation, three in series for each of the plant's two process lines, with a total of about 5 million t of ore having been prepared for leaching. One group of pits was producing from the upper three beds, and the other had two pits operating on the upper beds and one from the lower beds. Return brine from the plant at a concentration of 8–12% Na_2SO_4 (or freshwater when a pit became nearly exhausted) was heated to about 17°C and sent to the most completely leached of the pits at a flow rate of 90–110 m³/hr. It left the first (the oldest) pit at a concentration greater than 10% Na_2SO_4 (3–4% Na_2SO_4 when leaching with water alone); the second pit's exit concentration was 15% Na_2SO_4 , and that of the third, or least leached of the pits, was 18–20% Na_2SO_4 , 0.16–0.25% CaSO_4 , very little sodium chloride or magnesium sulfate, and at about 25°C. The sodium chloride concentration was kept low by carefully removing the underlying clay (which contained small amounts of NaCl) from each glauberite zone. The sodium sulfate recovery from the pits had averaged 80–90% to 1999, but it was felt that 95% recovery could be obtained as they improved the pit preparation and operation.

Strong brine from the pits was sent to the two parallel processing lines in the plant (Fig. 4.19), and first cooled by return brine in plate and frame heat

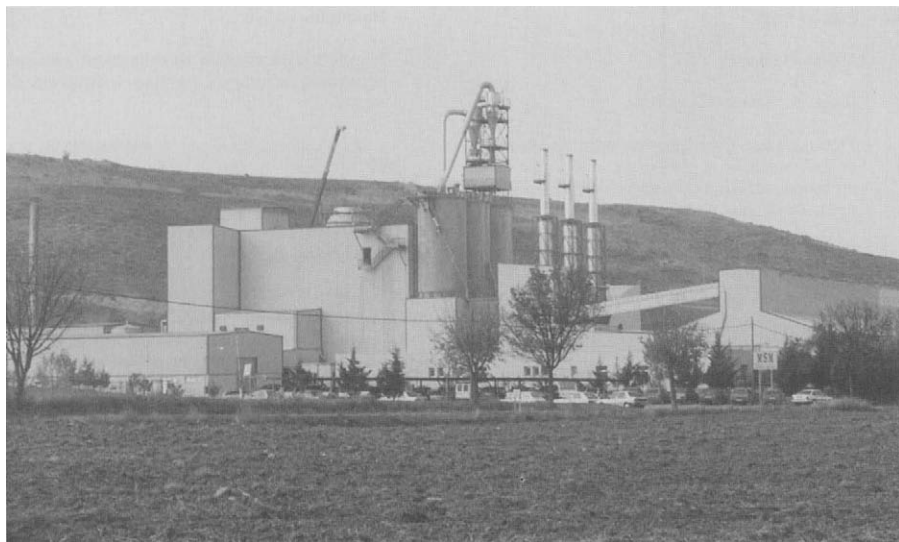


Figure 4.19 The Minera de Santa Marta (MSM) sodium sulfate processing plant. (From Regueiro *et al.*, 1997.)

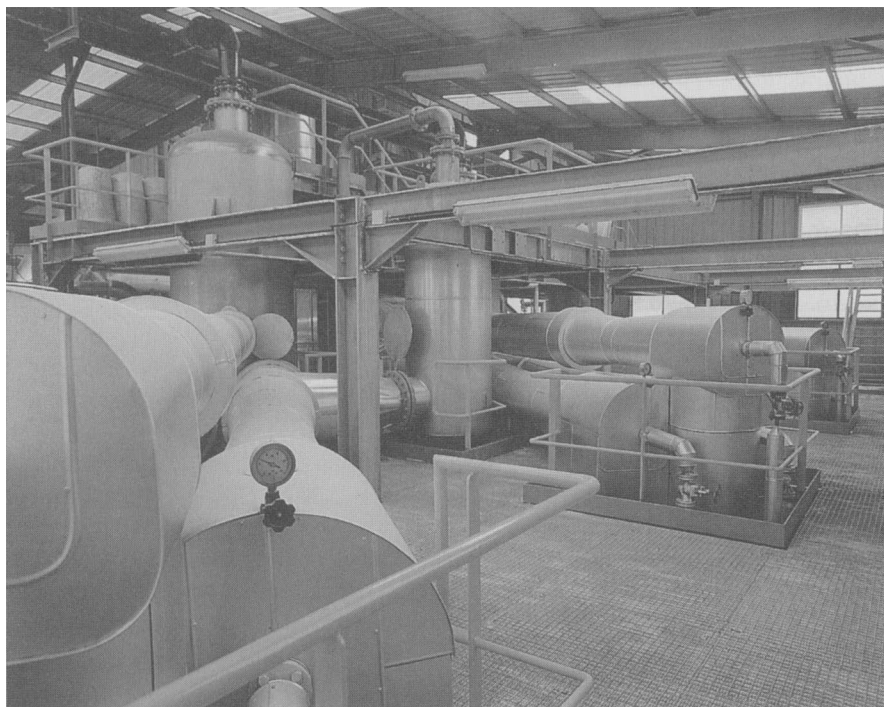


Figure 4.20 Steam-jet ejectors and barometric condensers at Minera de Santa Marta. (From MSM, 1997, courtesy of Minera de Santa Marta.)

exchangers. It next went to steam-jet (Fig. 4.20) evaporative crystallizers where it was cooled to 10–15°C to form glauber salt. The slurry from the crystallizers was thickened and then dewatered and washed in a two-stage pusher-type centrifuge. The centrate was returned to the thickener, and the thickener overflow was sent to the incoming brine heat exchanger. From there it was further heated by condensate from the evaporators and returned to the glauberite pits to commence an additional leach cycle. In the old plant the glauber salt was melted by the vapors from the third stage of a triple effect evaporator, the resulting anhydrous sodium sulfate solids were removed, and the residual brine was sent in parallel flow to the three effects of the evaporator. The evaporator required only a 2-hr washout on about a 15-day schedule, and condensate from the first two effects was flashed and sent to the third effect. Each effect was operated at a 50–55 vol% slurry density, and solids were removed, thickened, joined by the solids from the melter, and given a mild wash in a two-stage pusher-type centrifuge. The product centrifuge cake had a 4–5% moisture content and was sent to one of two steam-heated fluidized bed dryers, followed by similar coolers. Dust from each unit was dissolved and returned to the leaching pits because of its small crystal size and comparatively high impurity content.

In the new plant the glauber salt from the crystallizers was dissolved in condensate (rather than melted) in order to avoid forming smaller, widely sized crystals during melting. The nearly saturated solution was then sent to an Oslo-type vapor recompression evaporator (Fig. 4.21), a unit that is designed to produce large and uniform crystals. The very high brine circulation rate through its 15-m-long heat exchanger (with 1100 titanium alloy tubes) produced only a 1.5°C temperature rise, which resulted in very gentle supersaturation conditions in the tubes and piping before it flashed and boiled in the evaporator. There was also a high circulating slurry density to minimize nucleation during boiling, and a comparatively long residence time in the underneath holding vessel to relieve any remaining supersaturation. As a result of these features the unit did not tend to become fouled (by crystals growing on the walls), and heater washouts were required only about once per year. The unit also produced a large (predominantly 500 or 600 micron; 32 or 28 mesh), uniform, and pure crystalline product. A slurry was constantly withdrawn from the evaporator, thickened to 50 vol%, centrifuged and washed, and then sent to a fluidized-bed dryer-cooler. The product from both plants was screened and then segregated

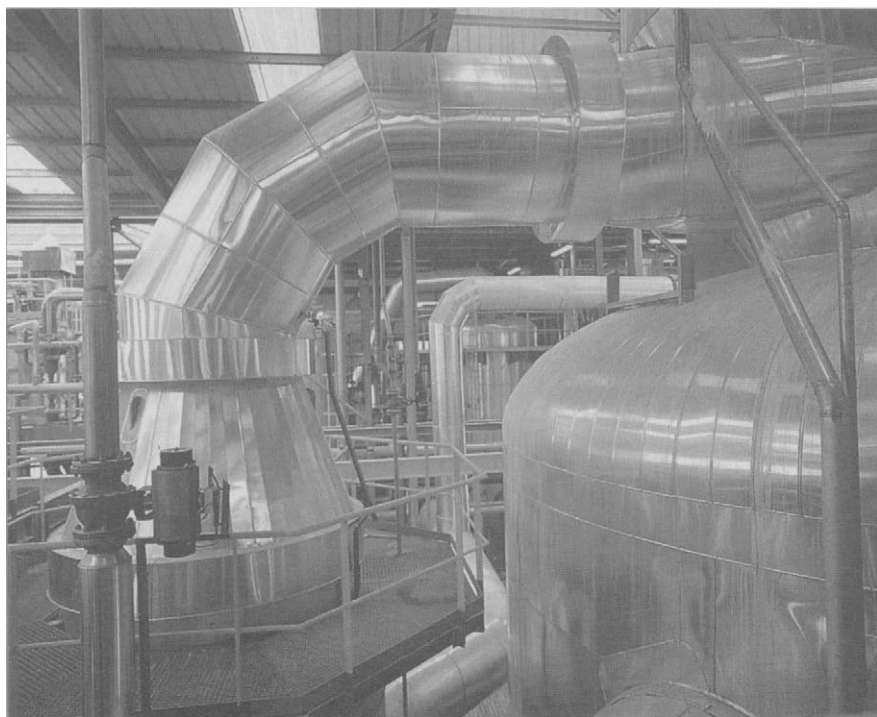


Figure 4.21 Piping from the heat exchanger to the top of the Oslo-type evaporator at Minera de Santa Marta. (From MSM, 1997, courtesy of Minera de Santa Marta.)

into standard, coarse, and granular grades, with the latter two having a very narrow size distribution, and none having any dust. A laser monitoring instrument automatically recorded the particle size range of the crystals. The product was shipped by truck to customers or the port at Bilbao in bulk, 25- or 50-kg bags on 1000-, 1250-, or 1500-kg pallets, or in 1000- or 1500-kg bags. About 85% of the product was exported.

The plant filled its water reservoirs in the winter from the nearby Tiron River, and drew little from the river during the summer (in dry periods it could even donate some water to the local farmers). The water had a low soluble solids and organics content and required no treatment before being used in the process. However, when the first plant was built a large soda ash (Na_2CO_3) precipitation section was added to remove calcium from either the water or glauberite leach liquor, but it has never been required because of the efficiency of the process. A large 20-MW diesel-fired cogeneration power plant was also later built that provides steam and power to the plant and sells its excess electricity to the local utility company. In 1999, 64 people were employed in the operation, including mining (most of this was done by a contractor), sales, administration, and operations. The mine had an operating staff of 1–2 (mainly for sampling and brine control), the laboratory had 2 chemists, and there were 5 engineers (2 in production, 2 in maintenance, and 1 in management). There were no environmental problems, and most of the land that had been reclaimed by 1999 was leveled (forming plateaus where there had previously been less useful rolling or steep hills) and appeared to grow excellent winter wheat (Antonio Cejalvo, 1999; Javier Alvarez, 1999).

S.A. Sulquisa

This operation is in the Madrid Basin and is the only Spanish company to produce sodium sulfate from a single, very thick, uniform glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$) ore body by an open pit, *in-situ* process. After several years of prospecting and process development by a joint venture of Minerales y Productos Derivados S.A. (Mineresa) and Industrias Penoles of Mexico, production commenced in 1982 with a modern, large-scale operation. The initial 90,000 mt/yr plant was reported to have cost \$8 million and in 1983 employed 22 people. In the process they first removed the 15–21 m of overburden from the ore that was to be leached, but left enough around the margins of the pit to contain the glauberite after it had been expanded. The first of the *in-situ* leach pits were about 100 by 100 m in size, as deep as the ore thickness (nominally 25 m), and had a ridge (baffle) in the middle to force the leach liquor into a longer flow path (Fig. 4.22). The ore was then drilled and blasted to fragment it and provide porosity for the leach liquor, and injection and withdrawal wells were installed. The pit was next filled with water, and brine circulation pumps assisted the leaching of the ore. Two pits were operated in series in 1989, and a nearly concentrated (up to 20% Na_2SO_4) brine was removed and sent to the plant. There it crystallized glauber salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) by being cooled to 15–18°C in the summer, or 11–12°C in the winter, from the boiling created by six stages of

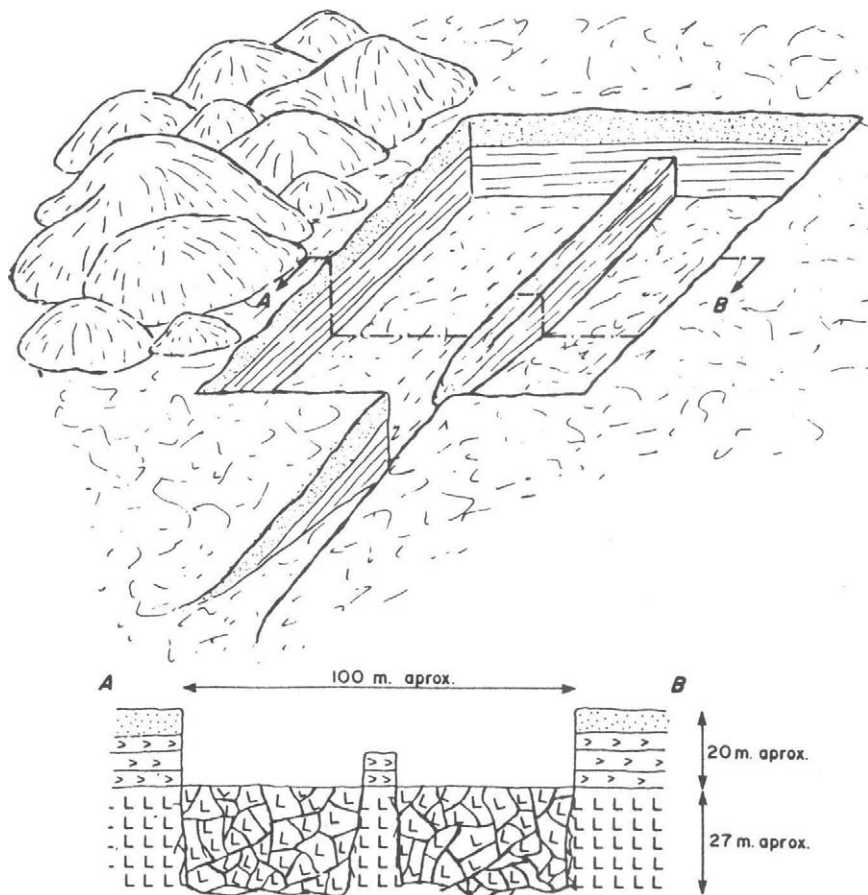


Figure 4.22 Diagram of the initial glauberite leach pit utilized by S.A. Sulquisa. (From Ordonez *et al.*, 1982.)

progressively higher vacuum. The glauber salt was then thickened, centrifuged, washed, melted, and sent to a triple-effect evaporator, while the residual $\sim 9\%$ Na_2SO_4 brine was heated to 35°C and returned to the leach pit. A slurry of anhydrous sodium sulfate was continuously withdrawn from the evaporator, centrifuged, and dried at 150°C in a fluidized bed dryer. A bleed stream from the evaporators was returned to the pit or processed separately. The high-purity product ($99.7\text{--}99.8\%$ Na_2SO_4) was next screened, sent to a storage silo, and shipped by truck directly to the customers, or for export to the port of Bilbao in bulk, bulk bags, or 50-kg bags (Ordonez and del Cura, 1992; Coope, 1983; Ordonez *et al.*, 1982).

By 1999 the production had been expanded to 200,000 mt/yr of an even higher grade sodium sulfate by the installation of a second parallel line of processing

equipment, and with a total of nine glauberite insitue leaching pits (locally called ponds). At that time the recoverable ore reserves were estimated to be 20 million mt of 25–45 m thick glauberite averaging 39% Na_2SO_4 , and covered by 25–40 m of overburden. Not included in the reserves were ore beds that bottomed about 100 m beneath the surface. The ore contained an average of about 1% NaCl and 1% MgSO_4 (the latter largely in the form of astrakanite) and rested on an impervious layer of clay. The leaching pits were prepared as needed by contractors, and the new ones were nominally 200 m long and 100 m wide, depending on the configuration of the mining layout and the shape of the ore body. After the overburden was removed, a 20- to 30-m wide trench the thickness of the ore body was dug along one of the long sides of the pit to provide additional free surface and expansion room for blasting the ore. The ore was then blasted to provide a 20–25% porosity in the pit, and the previously mined ore placed either on the top of the blasted ore, or in another pit. A series of brine (or water) injection wells were then placed along one of the pit's long sides, with their discharge about 10 m above the pit's bottom. Recovery wells were placed along the opposite side, withdrawing from the pit's bottom (Fig. 4.23). A new pit would first be filled with water, and later when an old pit had experienced about an 85% sodium sulfate recovery it would be removed at the same time and its drainage brine also sent to the new pit. The eighth pit was constructed in 1996 with ore 45 m thick; the ninth pit was not yet in use during



Figure 4.23 Glauberite leach pit and pumping station at Sulquisa. (Courtesy of S.A. Sulquisa.)

1999 and had ore 35 m thick. The nine pits at that time contained a total of more than 2 million t of sodium sulfate.

The dividing barriers in the first six pits were later blasted into porous ore, combining their adjacent sections into three larger pits. As the blasting technique was being developed the first two pits suffered considerable short-circuiting during leaching, so these combined pits were operated separately by being flooded and a dredge providing additional brine circulation within the ore. The other four large pits in 1999 were operated in series, with the brine level maintained about 4 m below the surface until a pit was nearly exhausted, and then the level was raised. The recycled brine from the plant to the pits contained about 6–7.5% Na_2SO_4 , 6% NaCl , and 2–2.5% MgSO_4 , and entered the most nearly exhausted pit at about 34°C in the summer and 25°C in the winter (averaging about 30°C). It left from the newest of the pits with a concentration of about 18.5% Na_2SO_4 and a temperature of 24–26°C, and the brine was sparkling clear. The blasted ore in the pits was originally at a temperature of 12–15°C, and the rocks retained their shape, structure, and porosity during the leaching process.

In the plant (Fig. 4.24) the brine from the pits was first sent to a storage tank (where its temperature could rise to 27–28°C in the summer), and then to a Lurgi-type six-stage crystallizer. This unit is a large horizontal cylinder that has internal baffles dividing the brine flow into six compartments. Each compartment has a different liquid level resulting from an increasingly higher vacuum (which also causes vigorous boiling in each stage), created by large steam-jet ejectors operating above each section. The brine cools on a typical summer day from 28 to 25°C in the first stage, and then to 21, 19, 18, 16, and 14°C in the following stages. This crystallizes glauher salt to form about a 25 vol% slurry in the final stage, which is separated from the cold brine in a thickener. The thickener's underflow is further thickened in a cyclone, and then fed to a two-stage pusher centrifuge. The overflow brine and centrate is used to condense the second stage's boiling vapors (and those from a steam jet) in a barometric condenser, thus utilizing its cooling effect and heating it before being returned, along with make-up water, to the leaching pits. In a similar manner, the washed glauher salt from the centrifuge is repulped in its melted brine and sent to condense the vapors from the crystallizer's first effect (along with steam from a steam jet). This also provides cooling and acts as a melter (at 33–36°C) for the glauher salt. The vapors from the third through sixth effects of the crystallizer are condensed together in a single large barometric condenser that is cooled by cooling-tower water.

The slurry from the glauher salt melter, along with thickened solids from the evaporator, is cycloned, and the underflow solids sent to a two-stage pusher centrifuge (near, and identical to, that for the glauher salt, with a spare centrifuge being maintained between them). The centrate and the cyclone overflow are heated by the evaporator's condensate and sent to the evaporator's settler. Its overflow becomes the evaporator's feed supply, and the underflow is again cycloned. The cyclone underflow joins the melter slurry, and the overflow returns

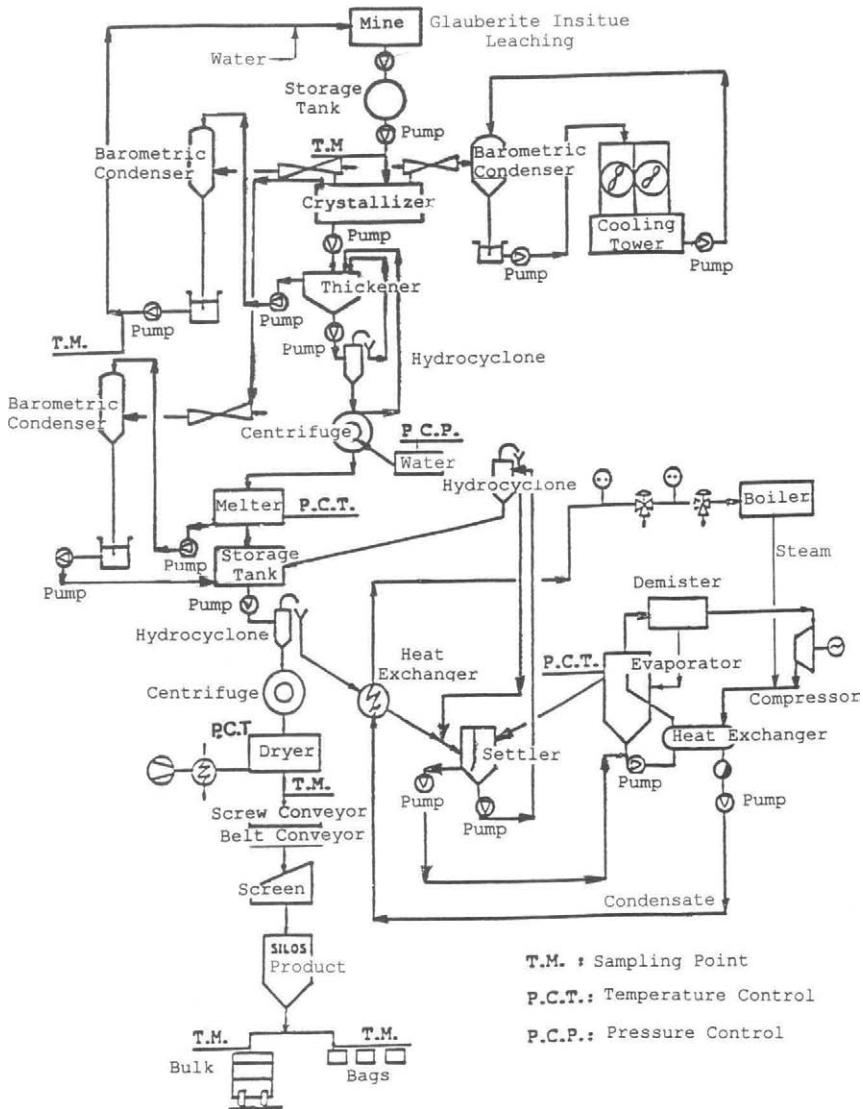


Figure 4.24 Process flow sheet for the Sulquisa sodium sulfate plant. (Courtesy of S.A. Sulquisa.)

to the settler. In the new plant the evaporator is a vapor recompression unit, operating with a 40 vol% slurry density, the compressor rotates at 15,000 rpm, and an efficient demister is located between the evaporator and compressor. The product is washed in its centrifuge, and the cake with 4–5% moisture is then conveyed to a fluidized bed dryer where its moisture is reduced to about 0.01%. It



Figure 4.25 Loading station at Sulquisa, with the plant in the background. (Courtesy of S.A. Sulquisa.)

is next screened, sent to silos, and shipped to the customers by trucks in bulk (Fig. 4.25) or bags.

All operations in the plant and pits are controlled from the central control room, based on the staff's own development of the control software. The operation also has two 4.5-MW gas turbine power plants with heat recovery boilers to provide steam for the plant's needs. Every 4000 hr a turbine is taken off-line for maintenance, and each of the units is washed once per month. Excess power over that required by the plant is sold to the local electric company as an added profit source. In 1999 the operation had a staff of 31, including four engineers and three people in accounting, and operated 24 hr/day, 365 days/yr. The plant had no environmental problems, and

when the ponds were completely extracted they would be filled with overburden and returned to their original condition. Areas with overburden already in its final position have been planted with pine trees that are being watered until they can survive on their own (Galdon, 1999; Navarro Munoz, 1999; Gonzalez Lastre, 1999).

Some of the Minerales y Productos Derivados S.A. patents provide an additional insight into the *in-situ* leaching technology of glauberite. As noted, their ore contains variable but significant amounts of sodium chloride and magnesium sulfate. In one example (Minerales & Productos Derivados [M. & P.D.], 1981) single-pass leach liquor contained 0.93% NaCl and 0.79% MgSO₄, quantities that lowered the maximum theoretically obtainable sodium sulfate concentration in the leach liquor from about 24.3% to 21.7% at 30°C. The maximum leach brine concentration was reached at about 27°C, the temperature at which both decahydrate and anhydrous sodium sulfate were saturated. Once the liquor is separated from the gypsum and glauberite in the ore, a 30°C leach solution with 20% Na₂SO₄ when cooled would be saturated with glauber salt at about 25°C, which is often above the ambient temperature. To lessen the chance of glauber salt crystallizing in pipes or near the surface of the pit, the brine could be kept above this temperature, which would also increase the rate of leaching (i.e., at 35–40°C the rate is 2–3 times that at 25–30°C), but the sodium sulfate concentration would also drop (see Fig. 7.10). In small single-pass laboratory packed columns (M. & P. D., 1981), when the leach liquor concentration reached 17–19% Na₂SO₄ only 50% of the sodium sulfate in the ore had been leached. To recover 75% of the sodium sulfate the leach solution only reached 13.5% Na₂SO₄, and at 85% recovery the brine contained only 10% Na₂SO₄. Thus, to obtain both a reasonable recovery (i.e., >80%) and a high brine strength (15–20% Na₂SO₄), they recommended that there be at least three chambers leached in series before the initial chamber is adequately depleted and removed. The patent also suggested ultimately blasting and leaching the ore lost in the walls between the chambers. Finally, Plaja Tarres (1994) proposed dredging the residual ore from an improperly blasted leach vat and releaching it, or using an internal venturi mixer in the vat (as is apparently being done in Sulquisa's first pit). A number of other patents have been issued on glauberite leaching, such as by Lluís Pellisa and Palja Tarres (1993), Navarro Munoz (1981), and Plantalamor Rovira (1981).

Crimidesa

The first company to practice *in-situ* leaching of comparatively thin glauberite ore beds was Crimidesa at *Cerezo de Rio Tiron* in Burgos province, at a site just north of the MSM operation. Underground mining with plant leaching had been employed for about 40 yr, but the operation was changed in 1980 to an *in-situ* process. The overburden and upper glauberite bed were first removed, and a leach pit prepared in the second [B] ore bed, generally being about 200 m long, 75 m wide, and 8 m deep (the thickness of that bed among the six present in their area). A drainage canal was then made along the 200-m side, "horizontal bore holes" constructed, and a wooden structure filled with coarse rocks placed in the canal to help distribute the

incoming brine. Vertical bore holes were then drilled along the entire perimeter of the pit and the ore was fragmented by explosive blasts. The pit was next filled with brine that was circulated through the broken ore until nearly saturated, and it was then withdrawn and sent to the plant. The brine's flow rate and strength were carefully controlled to reach a high concentration, but not high enough to crystallize glauber salt in the pipes during the winter. The brine was then cooled in a tower by a countercurrent flow of air to crystallize glauber salt. The solids were hydrocycloned and centrifuged, and then dehydrated in multiple effect evaporators to form anhydrous sodium sulfate. The overflow brine and centrate were next heated and returned to the pit (Menduina *et al.*, 1984; Ordóñez *et al.*, 1982).

FMC Foret

The oldest of the Spanish sodium sulfate operations is the *El Castellar* thenardite mine and plant at Villarrubia de Santiago in Toledo province, now owned by FMC Foret. The 5- to 8-m thick (5–6 m, Rovira, 1960), predominantly thenardite (Na_2SO_4) ore bed (with some glauberite [$\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$], magnesite [MgCO_3], and clay) was entered from a tunnel cut into the red shale under the thenardite outcrop. This served as the haulage level, ventilation entry and exit, and the entry for all of the services (electricity, water, etc.) for the mine. Raises from this adit were made to connect to the mining level, where the mining was done by a room and pillar stoping procedure, mining down from the top. The mining plan provided for mining ore that was up to 9–10 m thick, from the thin overlying mirabilite to the underlying glauberite, with the floor established in the underlying halite bed. The pillars between the stopes were 3 m thick, and when the ore was sufficiently thick up to 3 m could be left in the ceiling as a stronger roof beam. Two stopes were mined at the same time, usually being 140 m apart. The mined ore was dropped to the haulage level, and then conveyed to the plant (Ordóñez and García del Cura, 1992; Ordóñez *et al.*, 1982).

In the processing plant the thenardite–glauberite–mirabilite ore in 1960 had an analysis of 70–75% Na_2SO_4 , 11–17% CaSO_4 , 3–9% other insolubles, 1–5% water, and 0.4–0.6% NaCl . It was first ground to the desired size in a hammer mill and sent to storage silos. From there it was initially leached at 50–60°C in agitated tanks, but as the clays in the ore were converted from the calcium to the sodium form they tended to peptize into a colloidal state that made them almost impossible to settle or filter. This problem was solved by loading the ore into one of six tanks to be leached as a fixed bed, four-tank, countercurrent system operating at 35–40°C. A sparkling clear, nearly saturated solution was produced (with 4–5 g/liter CaSO_4), but the sodium sulfate recovery was only 40–45%. One of the six leach tanks was always being loaded, and another unloaded of its leached residue. This residue, containing the remaining thenardite and all of the glauberite and insolubles (45–50% Na_2SO_4 , 30–35% CaSO_4 , 20–26% insolubles, and 0.3% NaCl) was then sent to a ball mill to be ground to a smaller size. Its discharge was next sent to a series of six 5-m diameter, 5-m high agitated leach tanks that were kept at a temperature of about 29°C with cooling water. From there the leached slurry was pumped to a

15-m diameter, 2.7-m tall settler, and the clarified overflow liquor, containing less than 20% Na_2SO_4 (the maximum glauberite equilibrium concentration), was returned to the thenardite dissolving tanks. The residue of gypsum and insolubles was washed by water introduced into the base of the settler and discarded with a sodium sulfate content of 5–7%. The overall leaching yield was said to be 85% (Fig. 4.26).

The hot thenardite leach liquor was next given a polish filtration and sent to three parallel single effect thermocompressor (compressed by jets of 176–220 psi steam) vacuum evaporators. The brine was circulated through these units' heat exchangers and evaporated at 70°C to crystallize anhydrous sodium sulfate (Fig. 4.27). The evaporator's steam was condensed by either heat exchangers in the leaching circuit or barometric condensers, both assisted by vacuum pumps to remove the non-condensables. The crystallized product was continuously removed, and thickened, centrifuged to a 6–7% moisture content, and dried. The product, at a production rate of 30 mt/day, was sent to silos and shipped, averaging 99% Na_2SO_4 , 0.6% NaCl , 0.3% CaSO_4 , and 0.2% H_2O . The total ore reserves in 1960 were 200 million t, including 60 MMt of more easily mined ore (Ordóñez *et al.*, 1982; Rovira, 1960). Over the many years that the plant has been in operation the mining has become much more difficult and the grade of the ore has been reduced.

Other Mines

In the same general area of Spain there are also two abandoned mines. The *Vicente*, near Ciempozuelos, was shut down in 1968, with only 50 t of production that year. The *Comfort* mine utilized a room and pillar mining operation and was closed in 1936 (Ordóñez and García del Cura, 1992).

Turkey

There are three playa-lakes in Turkey from which sodium sulfate is recovered: Acigol, Tersakan, and Bolluk. The basic method of production from each of them had been to first pump surface brine (often supplemented by spring, aquifer, or interstitial brine from lake wells or seepage trenches) in the summer into solar ponds or smaller subdivisions of the lake. The entering brine concentration was monitored so it would not be pumped until it was strong enough that it would not excessively dissolve the permanent 20- to 30 cm layer of mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$)–thenardite (Na_2SO_4) left in the ponds as a clean floor for the later harvesting of thenardite. During the summer the pond brine was also monitored and fresh brine added to prevent halite (NaCl) from crystallizing. As the concentrated brine cooled from the end of October to the end of December it crystallized mirabilite, forming a layer up to 50 cm thick in the center of the ponds. From January through early spring the residual brine (initially) and later rainwater in the ponds was drained and pumped back to the lake, allowing the mirabilite to be somewhat washed by the rains. This washing–leaching and the subsequent evaporation also helped to rebuild the thenardite–mirabilite floor that was partially dissolved the previous summer. The mirabilite was then slowly dehydrated in the ponds, and by

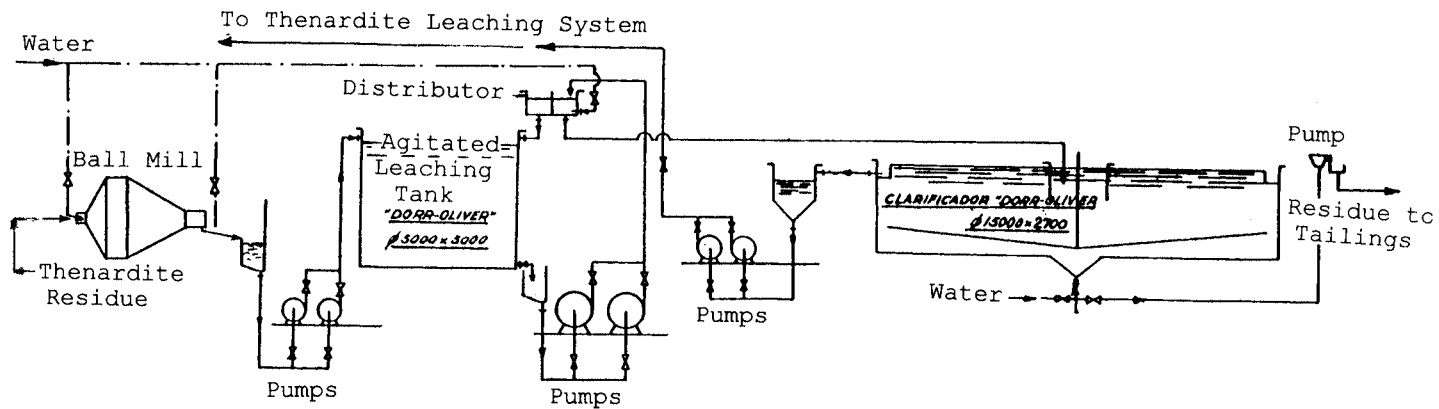


Figure 4.26 The early FMC-Forêt flow sheet for leaching their thenardite residue (mostly glauberite). (From Rovira, 1960.)

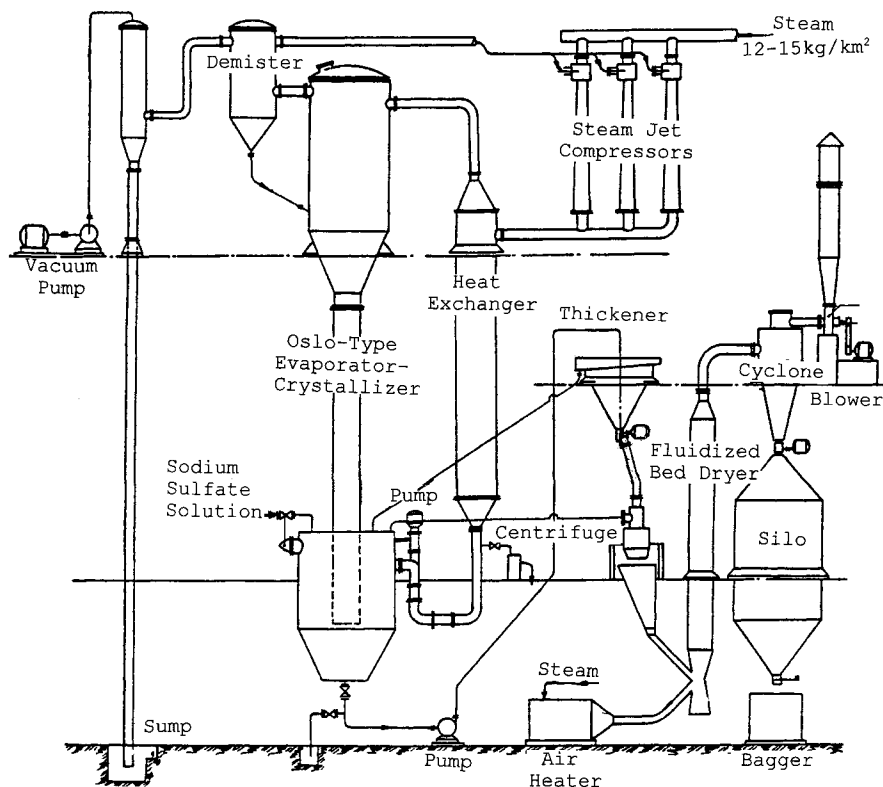


Figure 4.27 The early FMC Foret sodium sulfate evaporator-dryer system. (From Rovira, 1960.)

June of the second year it began to form a crude sodium sulfate product. During the summer it was frequently scraped from the ponds' surfaces and loaded into bags.

The mirabilite formed in the winter as either large, thin interlocking hopper crystals, or fine, radiating, acicular crystals. A cross section of the mirabilite crust often shows a thin layer of laminar thenardite-mirabilite crystals mixed with some astrakanite ($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$) on the surface, and under that massive "dog tooth" mirabilite crystals pointing downward (Fig. 3.32). Below that there is usually a thin layer of smaller equant mirabilite crystals, with the layer's lower zone mixed with a small amount of calcite (CaCO_3), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and mud. When the mirabilite dehydrates in the ponds in the summer it forms very small powdery crystals that can easily blow away. At temperatures above 32.4°C the mirabilite also "melts," leaving a residue of about 15% of its mass as thenardite, and a saturated sodium sulfate solution. This solution, and any other resulting from rain leaching, then crystallizes more thenardite at these elevated temperatures. This thenardite forms hard, compact, transparent crystals with a rhombic habit, which often contain some solid-phase inclusions.

Bolluk Lake

Normally at Bolluk Lake the production ponds are only used to form new mirabilite every 2 years unless the lake had received excess runoff and flow from the springs, and the summer had been hot and windy enough to have sufficiently concentrated the brine. The lake's brine supply is primarily from high-sulfate springs draining into the lake, which because of their limited flow also controls the amount of sodium sulfate production. These springs supply sufficient weak brine during the summer to dilute the brine in the mirabilite-forming ponds if needed to prevent sodium chloride from crystallizing. The rainfall in the area is obviously critical, since too much could flood the ponds or dilute the brine, and even a little in the summer could form a thenardite crust on the surface of the mirabilite and reduce the dehydration rate. Light winds greatly aid the operation, but heavy winds can blow the product away and damage agriculture for many kilometers downwind. These problems have been balanced over the years, however, and successful production has taken place (to 1999) for ~50 yr (Gundogan and Helvacı, 1996).

Late 1990s Operations

The capital and operating costs for the operations are quite low, and the limited brine supply allows an average production of about 10,000 mt/yr of crude sodium sulfate from Bolluk and Tersakan Lakes. More than 100,000 t/yr was produced from the larger Acigol Lake (Icozu and Calakpkulu, 1993), and because of the increasing demand for a higher purity product, it has been reported that in the mid-1990s some of the mirabilite began to be harvested and then evaporated to form a more competitive product (Alkim, 1997). In the late 1990s some ore from the development mining of the thenardite–glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$) deposit at Beypazari was also being sent to Bolluk Lake for processing. Most of the country's production was consumed in Turkey, converted into sodium sulfide (Na_2S), or exported, primarily to nearby countries.

United States***Arizona: Western Chemical Co.***

The *Camp Verde* thenardite (Na_2SO_4) deposit had been mined by the native people of the area for salt, starting about 2000 years ago and then intensifying in the 14th and 15th centuries to form a labyrinth of rooms and tunnels at four or more levels in the lower halite beds. Much more recently some of the upper thenardite beds also began to be mined for their sodium sulfate content, with the first substantial production being as an open pit operation from 1920 to 1926 by the Western Chemical Company. An approximately 7-m-thick zone of thenardite was mined that had a comparatively thin overburden. Blast holes were drilled into the ore with hand-held drills, and after blasting the ore was loaded into horse-drawn carts by a small gasoline-operated power

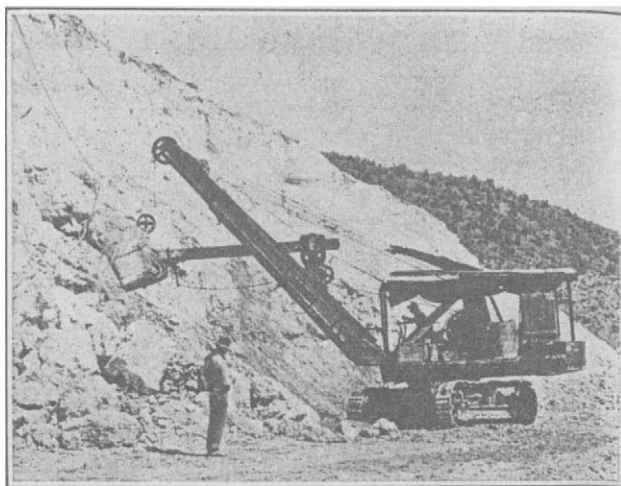


Figure 4.28 Gasoline-powered shovel at the Camp Verde thenardite deposit. (From McDermid, 1934, courtesy of *Engineering & Mining Journal*.)

shovel (Fig. 4.28). Some of the halite (NaCl) impurity in the thenardite was then removed by handpicking, with the halite being sold as cattle salt. The ore was next passed through a grizzly and ground to -3.8 cm (later: -1.9 cm first, then stored, and at the end of processing ground to the product size [at that time] of -5 mm; Cole, 1926; Anon., 1924) in a Jeffrey crusher. Following the initial size reduction it went to two log washers in parallel, each followed by a second one in series, with a countercurrent flow of Na_2SO_4 -saturated, NaCl -unsaturated brine. The agitation in the washers dislodged and suspended much of the insolubles, and dissolved most of the halite. The fine, reject slurry from the log washers was sent to a settling pond, and the clear liquor from it, along with ~ 167 gpm of make-up water, was returned to the system. The washed coarser solids were sent to a 2.4×15.2 m (8×50 ft) oil-fired dryer, and its discharge was initially screened at 6 mm. The undersize fraction was discarded, and the oversize sent to a roll crusher. From there the product was screened to form three grades ($+13$ mm, $6-13$ mm, and -6 mm) and sent to storage (Fig. 4.29). It was then hauled by truck 32 km to the rail loading site at Clemenceau.

The operation employed 40 men and produced 82–123 mt/day (2–3 carloads/day) of a $+95\%$ sodium sulfate product, containing 2% insolubles, 1.2–2% sodium chloride, $<1\%$ calcium sulfate, and 0.3% magnesium sulfate. Electric power to the plant was supplied by the Arizona Power Co. for its (combined) 190–202 HP of electric motors. Most of the product was sold to kraft pulp and paper companies (Young, 1927). In 1927 the plant was modified, but severe competition from German synthetic salt cake (from their HCl -producing Mannheim furnaces) caused the operation to shut down permanently that same year (Anon., 1933).

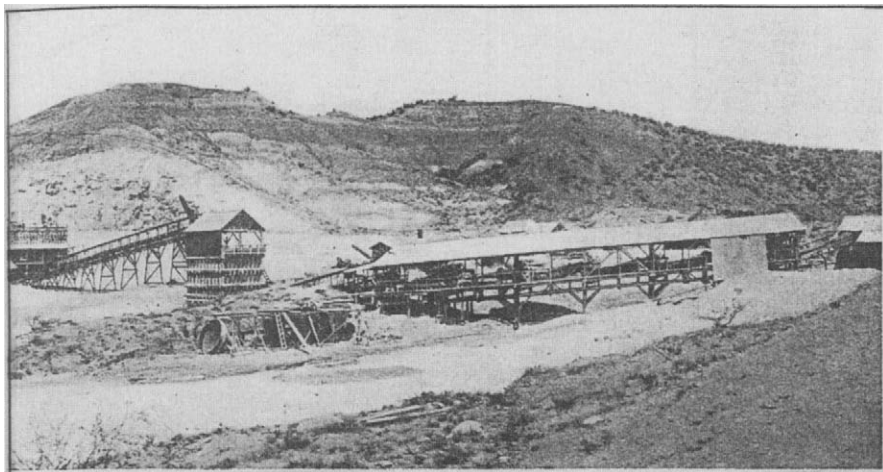


Figure 4.29 General view of the mining and processing facilities of the first Camp Verde operation. (From Young, 1927, with permission of *Engineering & Mining Journal*.)

Arizona Chemical Co.

The deposit was worked again from 1930–1933 by the Arizona Chemical Company, jointly owned by the American Cyanamid and International Paper Companies. This time, however, it was operated as an underground mine, entering the deposit in a high-grade 1.37-m (4.5-ft) flat-lying thenardite bed that outcropped along the west side of the Verde River valley. The ore was first cut by drifts into ~30 m square blocks, and then mined as open stopes of an unspecified height. Only comparatively small and irregular pillars were left (Fig. 4.30), and most of the drifts were untimbered. The blast holes were made by pneumatic drills, with up to nine being used together from a single compressor. After being broken, the stopped ore was removed by a 20-HP double-drum hoist pulling a hoe-type scraper. The ore was dragged up a wooden slide, and then dropped into 1-mt ore cars in the loading drift. From there it was hauled out of the mine by mules to a 200-t bin, and from there sent to the washing plant. Eventually 14 tunnels extended 150–180 m from the outcrops almost horizontally into the deposit. There was only one report of rock falls during the mining period, but in that incident a worker was killed while eating his lunch. Now the tunnels are mostly caved in and the timbers very delignified, and the remaining drifts are considered to be very unstable (Thompson, 1983).

The ore was next crushed to a -2.5 cm size and sent to a rotating cylindrical-screen washer made of two sections, the first 3.8 m long and 1.8 m in diameter, and the second 3.8×1.2 m. Water was vigorously sprayed against the tumbling rock, the fines passed through the 5 mesh screen openings, and much of the halite

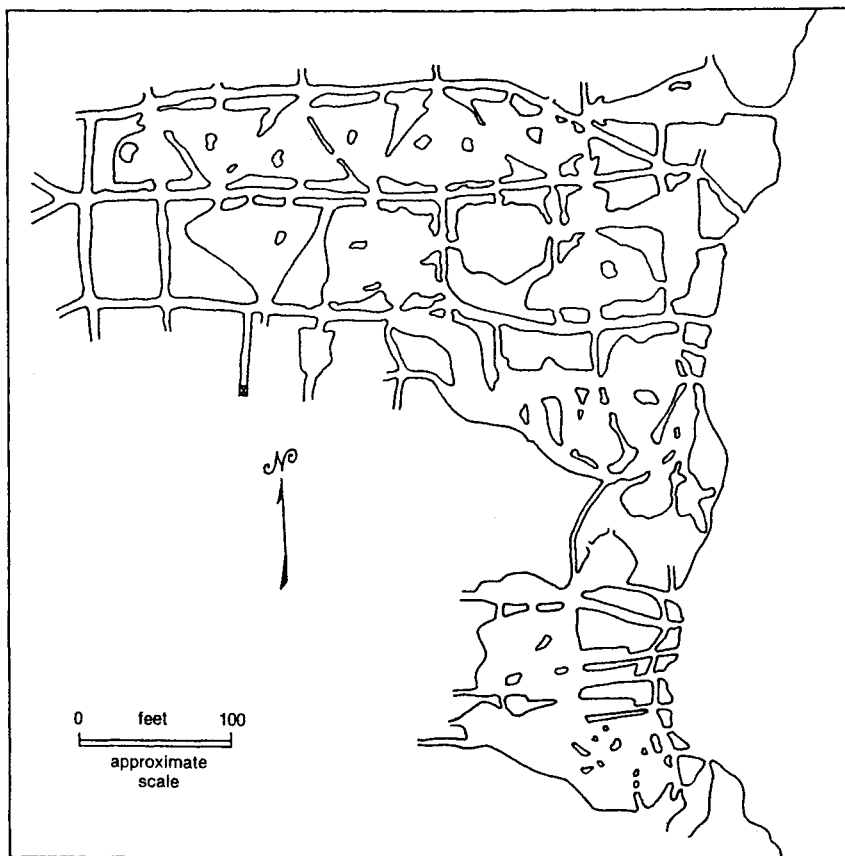


Figure 4.30 Map of the underground mine workings at the Camp Verde thenardite deposit. (From Thompson, 1983, with permission of *The Mineralogical Record*.)

dissolved. The coarse ore was then dried in an oil-fired 2.7×15.2 m rotary dryer, with most of the dust blown out in the flue gas and discarded. The dried product was next crushed in a 50.5×76.2 cm roll crusher to a -6 mm size and sold with a typical analysis of 95.14% sodium sulfate, 0.55% sodium chloride, 1.63% calcium sulfate, and 2.68% insolubles. About 70 men were employed in the operation (almost half of whom were Apache Indians), with the mine working three shifts, and the washing plant on a one-shift intermittent basis. The plant produced about 3000 t/mo (Tyler, 1935), and the product was trucked to the railhead at Clemenceau in 7-t trucks, to be sold primarily to kraft pulp and paper mills (McDermid, 1934). The operation was closed permanently at the end of 1933 because of its inability to meet the competition from lower-cost producers (Anon., 1933).

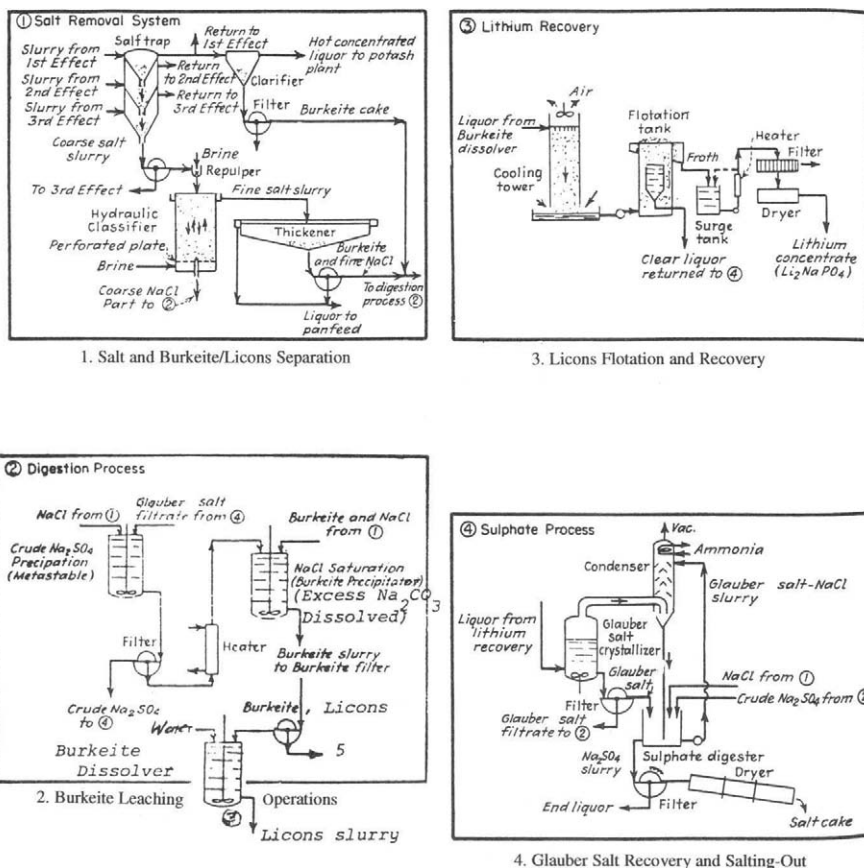
California: Searles Lake (American Potash & Chemical Corp.)***Winter Spraying***

Three methods of producing sodium sulfate from the brines of Searles Lake have been employed over the years, although only one is utilized at present. For many years they were the world's largest producer of sodium sulfate, with a capacity of over 500,000 mt/yr of Na_2SO_4 . The simplest of the production procedures was to spray upper structure brine into the air through 25 6.4-cm pipes (Fig. 3.35) whenever the air temperature was lower than about 5°C. The pipes were 6 m tall, spaced 9 m apart on the lake's surface, and had nozzles that formed a fine spray. As the brine cooled, falling through the air and flowing over the surface of the pile, glauber salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) was crystallized, forming a long terraced mound that in time built up to the height of the pipes. The runoff brine collected in an adjacent area and eventually seeped back into the lake slightly enriched in potash, carbonate, and borax. The glauber salt in the pile was harvested whenever the demand for sodium sulfate exceeded the plant's normal production capacity. It was picked up by front-end loaders, trucked to the Soda Products plant, and converted into salt cake by a salting-out process in the glauber salt crystallizer's repulp tank (with the salt produced in the main plant evaporators). A fairly high-quality, inexpensive product was thus obtained without adding extra equipment (Garrett, 1960).

Evaporation (Main Plant Cycle)

The major portion of salt cake that was formerly produced at Searles Lake was recovered from the plant evaporation of upper structure brine. The first evaporator plant on the lake was built in 1916 to produce potash; in 1919 borax production was added, then soda ash, and in 1940 salt cake. The lake's brine is a complex mixture containing about 35% dissolved solids (Table 3.18) and is saturated with all of the solid phase salts (including the sulfate minerals; Table 3.19) present in each zone of the deposit. Since the crystal and brine compositions vary somewhat, the wells were drilled in the most favorable locations for the products that were desired. A casing was cemented in the hole to within a short distance of the bottom, and pumps with 4.3-m (14-ft) suction capability were mounted in them. Initially a network of 70 pumps and piping brought the brine to the plants.

The plant evaporation process of the former American Potash & Chemical Corp. treated about 3 million gals of upper structure brine per day in a continuous, cyclic process. Brine was first mixed with recycle liquor from the borax plant, and evaporated to the potash saturation point. During evaporation, sodium chloride (>2000 t/day), burkeite ($\text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4$), and licons (NaLi_2PO_4) all crystallized with different crystal sizes. The salt was predominately >50 mesh, the burkeite <50 mesh, and the licons $2\text{--}5\text{ }\mu\text{m}$, so they were settled, hydraulically classified, and removed (Fig. 4.31, 1). Most of the coarser salt was returned to the lake, and the burkeite–licons mixture was sent to the Soda Products plant to recover its component salts. The clarified concentrated liquor was next cooled to 38°C (100°F) in gentle, growth-controlled crystallizers to form potash, which was recovered as the



plant's major product. The residual liquor was next seeded with borax to crystallize pentahydrate borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$), and after it was removed the end liquor was returned to the evaporators.

Two burkeite mixtures were recovered in the evaporator circuit, and they were separately filtered and given a brief wash. The major stream came from the clarifier (Fig. 4.31, 1) and contained mainly sesquiburkeite ($2\text{Na}_2\text{CO}_3 \cdot 3\text{Na}_2\text{SO}_4$), analyzed as 27.0% Na_2CO_3 , 40.7% Na_2SO_4 , 10.7% NaCl , and 21.6% water. The second stream came from the fines thickener for the salt classifier, and the two filter cakes were then combined. They were next partially leached by a cold low-sulfate process liquor (15.0% Na_2CO_3 , 7.5% Na_2SO_4 , 15.0% NaCl ; 30°C; Fig. 4.31, 2), and then in a second stage heated to 75°C. This decreased the solution's Na_2SO_4 solubility to 1.8%, and proportionately increased the amount of sodium carbonate (14.4% Na_2CO_3 and 17.4% NaCl). The leaching step recovered the mixture's small sodium

carbonate monohydrate ($\text{Na}_2\text{CO}_4 \cdot \text{H}_2\text{O}$) content (about 6.8% Na_2CO_3), while the heating converted the sesquiburkeite to burkeite, dissolved the salt, and crystallized more burkeite (it has an inverse solubility). The leach liquor then went on to the sodium carbonate recovery unit.

The remaining burkeite solids from the leach-conversion step were again filtered, and then dissolved at $\sim 27^\circ\text{C}$ (its maximum solubility temperature) in a low-calcium water (third effect condensate). The licons did not dissolve, and their thin slurry was cooled in two cooling towers before the licons were removed by froth flotation (Fig. 14.31, 3) and sent to another plant to produce lithium carbonate (Li_2CO_3) and phosphoric acid (H_3PO_4).

The clear flotation-underflow solution (containing 12.1% Na_2CO_3 , 21.2% Na_2SO_4 , and 1.5% NaCl) was sent to a glauber salt crystallizer (Fig. 14.31, 4) where it was cooled to 22.5°C (from 27.2°C) by the vacuum created in a barometric condenser. At this temperature a fairly high yield of glauber salt could be obtained without crystallizing sodium carbonate decahydrate (the sulfate to carbonate ratio in the brine was reduced from about 2/1 to 1/1). The glauber salt slurry was constantly withdrawn from the crystallizer, centrifuged, and washed. It was then repulped with crude salt cake from elsewhere in the process, and with salt from the evaporators. This converted the glauber salt to anhydrous sodium sulfate and leached salt from the crude salt cake, and the cooling effect from melting glauber salt formed a "eutectic" mixture at 16.4°C . This slurry was circulated through the barometric condenser to provide 85% of the cooling load for the glauber salt crystallizer (the remainder came from ammonia refrigeration), thus greatly reducing the energy required for the operation. A stream of salt cake was continuously removed from the repulp tank, and it was filtered, washed (and blown with steam), dried, and sent to the product silos. The salt cake filtrate was returned to the lake.

The cold glauber salt filtrate from the crystallizer (16.3% Na_2CO_3 , 14.1% Na_2SO_4 , 2.2% NaCl) was next sent to a second salting-out crystallizer system. Here it was closely temperature-controlled to below 21°C in the first three tanks in series, and then heated to $26.7\text{--}29.4^\circ\text{C}$ in the fourth tank. It was also heavily seeded with salt cake, and salt from the evaporators was added in increments to each of the tanks. Without the seeding the salt would have crystallized burkeite from the solution, but with the seed the mixture could be kept in a metastable state where only sodium sulfate (and a little sal soda [$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$], which later dissolved) crystallized. Careful process control and freedom from burkeite seed had to be maintained or the slurry could revert to burkeite (and have to be totally dumped, washed, and started again), but such a conversion was rare, and normally a fairly pure salt cake could be produced. It was continuously removed and filtered, and the cake was sent to the glauber salt repulp tank. The filtrate (now considerably enriched in sodium carbonate and depleted in sodium sulfate; 14.6% Na_2CO_3 , 7.2% Na_2SO_4 , 14.3% NaCl) was heated and sent to leach the entering high-sodium-carbonate sesquiburkeite, and in turn precipitate more burkeite, as previously noted (Garrett, 1992, 1960).

Carbonation Plant Brine

The third process for recovering sodium sulfate from Searles Lake brines was the final step in a series of manipulations beginning with carbonating the brine. This process was initiated in 1946 in Trona, in 1957 at the West End plant of the *Stauffer Chemical Co.*, and was expanded in 1976 at West End using end liquor from the new very large Argus soda ash plant (both operations were then owned by the Kerr-McGee Chemical Co.). The first 400 t/day West End salt cake plant set the present-day standard for quite pure, very white, uniformly sized sodium sulfate for all uses (including kraft paper), and thus slowly forced most other operators to meet their product quality. Lower structure brine, with its richer borax and sodium carbonate content, was first introduced into the top of large carbonating towers. There it was contacted by compressed carbon dioxide-containing gas distributed into the base of the towers, with the make-up CO_2 (most of the CO_2 was recycled from the sodium bicarbonate calciners) coming from flue gas at Trona, lime kilns at West End, or an MEA unit at Argus. Trona employed spray towers, while West End's towers, 22.9–24.4 m high and 1.5–3 m in diameter, contained sieve plates. The plates reduced the bubble size and provided a more even gas distribution in a countercurrent flow. At Argus the gas is dispersed by agitators in large single-stage tanks. The absorbed CO_2 converts the Na_2CO_3 in the brine to NaHCO_3 , which is only slightly soluble in the NaCl -saturated brine and so crystallizes. It is then removed, centrifuged or filtered, and sent through equipment to convert it to high-purity dense soda ash. The carbonated brine (with its acidic pentaborate $[\text{Na}_2\text{B}_{10}\text{O}_{16}]$ content) is next blended with fresh lower structure brine (containing the more alkaline metaborate $[\text{Na}_2\text{B}_2\text{O}_4]$) to form the less soluble tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$; or borax). In the first West End plant the mixed brine was next cooled in 10 stainless steel heat exchangers from 29.4 to 15°C (85–59°F) and sent to three 15-m diameter agitated crystallizer tanks. Borax seed crystals were added, and a large crop of borax was formed, thickened, and filtered.

The remaining liquor was then passed in series flow through two lines of three 6.7×6.7 m agitated and cooled tanks. The cooling was done by an ammonia refrigerant inside highly polished (to minimize fouling) vertical stainless steel tubes (with U-bends at their lower end) hung inside the tanks. Glauber salt seed crystals were added to the brine as it was cooled from 15 to 5.6°C (59–42°F), and much of the sodium sulfate and some of the remaining borax crystallized. The final mixed slurry was sent to a hydroseparator where the coarser glauber salt settled, and the finer borax passed off in the overflow to be recovered in a thickener. Its cold overflow brine was then returned to the entering feed heat exchangers, while the glauber salt was sent to a multitrays classifier. The smaller crystals from it went to the glauber salt crystallizers as seed crystals, and the coarse crystals (>20 mesh) were pumped to a 4-m diameter flatbed filter. On the filter the crystals were washed and given an air blow, and then conveyed to a 65.6°C (150°F) melter. The melted slurry was pumped to a double-effect stainless steel evaporator, and an anhydrous sodium sulfate slurry was constantly withdrawn at 60°C (140°F). The solids were thickened in a 9-m diameter

thickener, the overflow returned to the evaporator, and the slurry sent to two solid-bowl centrifuges. The centrate was sent back to the thickener, and the cake conveyed to a gas-fired rotary dryer operating at 135°C (275°F). As previously noted, compared to other commercial sodium sulfate of that period, a very high-purity, uniform, larger-sized, very white product was produced (Garrett, 1998, 1992, 1960; Chilton, 1958).

Late 1990s Operation

When the Argus plant came on stream in 1976 the Trona carbonation plant was closed. Then, on April 1, 1996, the operator at that time, the North American Chemical Co., shut down the main plant cycle and thereafter only produced salt cake from carbonation plant brine at West End. To partly make up for the lost capacity two changes were made: the brine flow rates were increased, and waste heat from a power plant's flue gas was used to preheat the brine returning from the plant and being injected into the formation to act as a warm "solution mining" brine. At the West End plant the 4000-gpm carbonation-borax-glauber salt plant's end liquor was heated to about 37°C (98°F), and the 3000-gpm for the carbonation plant (it formerly was 2000 gpm) and the 1000 gpm (it was 667 gpm) blending brine for the borax-glauber salt plants was withdrawn at about 27°C (80°F). This was a 6.7°C (12°F) increase, which considerably increased the brine's Na_2CO_3 and $\text{Na}_2\text{B}_4\text{O}_7$ content, and somewhat its Na_2SO_4 concentration.

Spent brine from the Argus carbonation plant was sent to West End and blended with lake brine to a pH of 8.3–8.5. This mixture was first cooled with cooling tower water, then with glauber salt end liquor at 16.4–16.7°C (61.5–62°F), and finally with ammonia coolers to 18.3°C (65°F) to crystallize borax. The borax was separated in a thickener, and then centrifuged and washed in three two-stage, 700-mm pusher-type centrifuges. The centrate and clarified brine from the thickener was sent to the glauber salt crystallizers (Fig. 4.32) for further cooling. The glauber salt with its borax content was removed and separated as in the earlier plant, and the glauber salt melted and evaporated to produce a quality product. Six 1000- to 1500-t ammonia compressors were used for the combined cooling load, with Evapco cooling towers containing 1.2-m (4-ft) ammonia condensing coils. The plant also converted brackish to fresh water by reverse osmosis and had a 19-MW gas turbine with a waste heat boiler and the injection brine heaters (Garrett, 1998).

Texas (Ozark-Mahoning Co.)

Monahans, Texas

One of the older and more unusual of the U. S. sodium sulfate producers was the Ozark-Mahoning Co. They and their successor companies have processed the strong sodium sulfate brines from several locations in northwest Texas (and briefly in southeast New Mexico) by a series of novel processing methods since 1933. Their success in this highly competitive field has been due to (1) a relatively favorable geographic location close to transportation facilities and the markets, (2) a plentiful high-sulfate brine supply at a shallow depth, (3) the availability of low-cost natural gas and a low-capital-cost evaporation method that produced a fairly high-quality product,

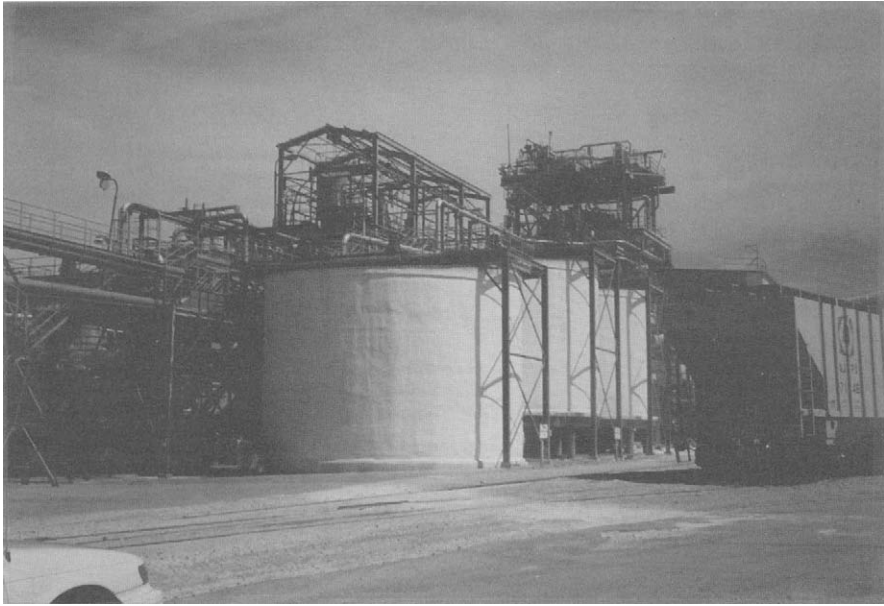


Figure 4.32 Glauber salt crystallizers at West End, Searles Lake. (Courtesy of IMC Global.)

(4) the availability of ample process water close to the plant (at Monahans, 3.2 km away), and (5) a good marketing program. Few other producers of natural sodium sulfate have had this combination of favorable commercial factors.

At Monahans there was a high-sodium-sulfate brine reservoir in an aquifer under a playa (Soda Lake) near the plant. The brine was pumped to the plant and cooled in scraped surface heat exchangers to crystallize glauber salt, which was then filtered, melted, and evaporated by submerged combustion to form anhydrous sodium sulfate. The deposit's brine was contained in porous sediments of the Ogallala Formation in an ancient closed basin and was pumped from two levels. Twenty-five 27-m-deep wells with electric submersible pumps were located on the playa surface, connected by a piping grid to transport the brine 2.4 km to the plant, aided by a high-pressure booster pump. In addition, an extensive but dilute 7–8% Na_2SO_4 brine was recovered from a depth of 18 m and pumped to solar ponds on the otherwise dry playa surface next to the well field. There it was concentrated in the summer to about 10% Na_2SO_4 before being pumped to the plant. The stronger (11.2% Na_2SO_4) but less plentiful brine in a tighter formation was used directly when the pond brine was not available. When the brine strength to the plant was below 11% Na_2SO_4 as much as one-third of it was first injected through a 305- to 457-m deep dual pipe solution mining system into a halite deposit to dissolve some of the salt. This increased the brine's NaCl content from 9–10% to 12–15% (saturation values),

thus greatly decreasing the mirabilite's solubility and increasing the crystallization yield when the brine was cooled.

Brine from the ponds or wells first went to a settler, and then a storage tank (both were made of wood, 9 m in diameter and 2.4 m high), and from there to the salt wells and a small plant-feed blending tank. The initial plant capacity was 100 t/day of Na_2SO_4 , providing a yield of about 0.9 lb Na_2SO_4 /gal of brine, with a flow rate of 9.5 liter/s (150 gpm). The brine was first cooled from its original 32°C temperature (90°F in the summer; 15.6°C [60°F] in the winter) to -6.7 to -9.4°C (15–20°F), requiring both heat exchangers and 500 t of refrigeration. This crystallized about 85% of the Na_2SO_4 as glauher salt (Fig. 4.33). The four heat exchanger units (12 exchangers in each unit) and three ammonia cooler units contained dual tubes, with the outer 20-cm (8-in) tubes containing either ammonia or return brine in counter-current flow. The brine to be cooled flowed through the inner 15-cm (6-in) tubes, which also contained a rotating spiral scraper to minimize tube fouling by the crystallizing glauher salt. After passing through the heat exchangers and one ammonia cooler the 1.7–4.4°C (35–40°F) glauher salt slurry became so thick that it was sent to a 6-m diameter thickener, and the glauher salt removed. The overflow brine (and the brine from the filters) was then pumped to the last two ammonia cooler units, and the final slurry sent to a second, 7.9-m thickener. From there the cold overflow (depleted) brine was sent through a group of heat exchangers, and then disposed of at about 12.8°C (55°F) onto the playa surface. The underflow from both thickeners was filtered, washed, and the solids sent to the evaporators. When the heat exchangers and coolers became fouled with crystals they were washed with dilute brine from the shallow wells, and the wash brine returned to the solar ponds.

In the initial period of plant operation the glauher salt was dehydrated by being sent to agitated tanks containing a warm Na_2SO_4 slurry, into which was immersed the lower section of steam-heated rotating drums. A layer of fluid stuck to the drums, traveled upward and out of the tank, was partially dehydrated and dried, and then scraped off by a knife blade and sent to a dryer. This cumbersome method was soon replaced by an only slightly improved process of melting, dehydrating, and drying the glauher salt in a long oil-fired rotating drum. Finally, in 1935 the filter cake began to be repulped by a stream of hot brine from product slurry settlers, and the resultant mixture was sent to new "submerged combustion" evaporators (Fig. 4.6). These units took advantage of the low-priced natural gas in the area (a clean-burning fuel) and low-cost construction. The fuel efficiency and particle size of the crystals that are formed are not nearly as good as those obtained in multiple effect or vapor recompression evaporators, but a fairly high-quality product could be quite easily produced.

In the evaporators combustion air was compressed to 7 psi by a 200-HP blower, blended with 170 cfm of gas at a slightly higher pressure, and burned under the liquid level in the polished 304 stainless steel vessels. The flame was ignited by an electrically heated incandescent wire, and flue gas then bubbled through the slurry, evaporating the brine and crystallizing anhydrous sodium sulfate. It was said that the flame temperature could be as high as 1427°C (2600°F), and that the flue gas

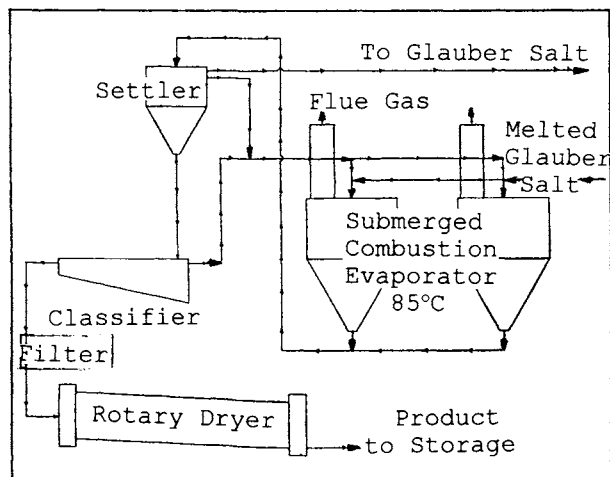


Figure 4.34 Evaporation and dryer flow sheet at Monahans, Texas. (From Weisman and Anderson, 1953, with permission of the AIME. First appeared in *Mining Engineering*, July 1953.)

classifier. Its 55% overflow slurry then went to a rotary dryer (Fig. 4.34), and the brine from both units was returned to the evaporator system as a repulping fluid for the entering glauber salt. The dried product had a purity of $>99\%$ Na_2SO_4 with less than 0.01% Fe, a screen analysis of $-10 +200$ mesh, and was “very white.” The company’s later-constructed *Brownfield plant* operated in a very similar manner (Weisman and Anderson, 1953; Anon., 1953), and both were closed by 1997.

Cedar Lake (Cooper Natural Resources)

The *Seagraves plant* of Cooper Natural Resources (formerly Ozark-Mahoning) produces from an aquifer under the quite similar Cedar Lake playa. In 1999 it operated with 55 wells into the aquifer, with usually only about half of them being required for an adequate brine supply to the plant. The wells were drilled to form 0.3-m (1-ft) diameter holes, 30 m (100 ft) deep and spaced about 50 m apart. A perforated (in its lower section) 15-cm (6-in) mild steel pipe was inserted nearly to the bottom of the hole, and then gravel was poured in the outer annulus to 12 m (40 ft) from the surface. A 0.3-m casing was then inserted in the 12-m open hole and cemented in place. Finally, a 30-gpm submersible pump was placed near the bottom of the 15-cm pipe in each well and connected to a 20-cm PVC piping manifold (Fig. 4.35). Near the center of the line of wells there was a small storage tank and a brine heater that was operated for about 4 months of each winter to heat the brine to $18\text{--}21^\circ\text{C}$ ($65\text{--}70^\circ\text{F}$), since if it cooled as much as 2.8°C (5°F) glauber salt could crystallize in the pipeline. A larger storage tank was located at the edge of the lake with a 75-psi booster pump to complete the approximately 4 km (2.5 mi) brine delivery from the wells to the storage tank in the plant. Because of the low pumping rate many of the wells have been in service for more than 30 yr without a



Figure 4.35 Brine supply pumps and piping at Cedar Lake. (Courtesy of Cooper Natural Resources.)

significant drop in brine concentration. Three additional older wells deliver a more dilute brine ($\sim 8\%$ Na_2SO_4) to a reclaim pond near the booster pump where reject sodium sulfate from the process is dissolved, settled, and returned to the plant. In the winter some brine spraying and glauber salt crystallization can also be conducted in this pond to provide a surge supply for the operation. Depleted brine from the plant is returned to the surface on the east end of the lake and forms a pool behind a small dike. Fresh water is supplied to the plant from wells 0.8 km to the west, and in a much higher aquifer than that in the lake (Frei, 1999; McIlveen, 1999).

From the plant's storage tank the brine is sent equally to five chilling units, each consisting of seven heat exchangers (Fig. 4.36). Four of the heat exchangers are cooled by spent brine, and three by ammonia (the latter are also called "chillers"). As at Monahans, each exchanger contains 12 10.7-m (35-ft) long, double (mild steel) pipe, internal rotating-screw heat exchangers, with all 12 screws of an exchanger driven by one 7.5-HP motor. The incoming brine first flows in series through the 12 15-cm diameter inner pipes (containing the scraping screws) of each of the first four heat exchangers, and countercurrent to the returning depleted cold brine from the last chiller (which flows through the 15- to 20-cm pipe annulus). The incoming brine is cooled from about 19.4 to 12.8°C (67 to 55°F) in the four exchanger units, and then flows to an ammonia-cooled chiller where it cools to 5.5°C (42°F). The approximately 5 wt% glauber salt slurry that has been formed is next sent to the first



Figure 4.36 Brine heat exchangers to the left; evaporator in the background at Cedar Lake, Texas. (Courtesy of Cooper Natural Resources.)

thickener, and its 30–40 vol% underflow slurry is pumped to a 30 m^2 ($2.3 \times 12.2 \text{ m}$, or $7.5 \times 40 \text{ ft}$) belt filter. The thickener's overflow brine and the filtrate from the filter is routed to a final ammonia-cooled chiller unit and cooled to the range of -1.1 to 1.7°C (30 to 35°F). The slurry that is produced is sent to a second thickener, and its underflow is also sent to the belt filter, while the overflow returns to the final heat exchanger of the first unit as its cooling fluid. The glauber salt cake is washed on the filter with chilled (4.4°C [40°F]) water, discharged with a 10% moisture content, and sent to the evaporator circuit. The exchangers and chillers are washed as necessary for about 1 h with 15.6°C (60°F) spent brine. The liquid ammonia enters the chillers at a temperature of -17.8°C (0°F) and 20 psi pressure.

The glauber salt filter cake is next repulped with 87.8°C (190°F) centrate from the anhydrous sodium sulfate centrifuges, and sent to a melt tank to be melted and further heated. The melter slurry circulates at 10,000 gpm through an exchanger heated by condensate from the evaporator, and then is sent to a hydrocyclone to thicken the anhydrous sodium sulfate that has been formed. The cyclone's underflow slurry drops to one of three (one is maintained as a standby) 250 t/d Baker Perkins single-stage pusher centrifuges (with no cake washing), while the centrate and cyclone overflow go to a vapor recompression evaporator (Fig. 4.36). This

evaporator was installed in 1985 and circulates a sodium sulfate slurry through its heater at a rate of 50,000 gpm. The heater has 2400 7.6-m (25-ft) long, 32-mm (1.25-in) OD titanium-nickel (Ticco 12) tubes, which do not corrode in the 1% NaCl brine of the evaporator. The vapor recompressor boosts the evaporator's exhaust steam at 0.5 psi to 5–6 psi for reuse in the heater, where it is joined by some new steam. A 20 vol% slurry is constantly withdrawn from the evaporator and hydrocycloned, and the underflow is sent to the anhydrous sodium sulfate centrifuges. The hydrocyclone overflow is returned to the evaporator, and no bleed is taken from the evaporator circuit. The centrifuged cake at about 5% moisture is delivered to a 2-m (6.67-ft) diameter, 12.8-m (42-ft) long, cocurrent gas-fired rotary dryer equipped with internal lifters for better heat transfer, and external knockers to minimize scale buildup.

The product from the dryer passes through a screen and is then sent to silos. From there it is delivered by a fleet of four 20-t dump trailers (Fig. 4.37) to rail loading stations at Seagraves and Brownfield, and bagging facilities at Brownfield. The plant has 50 employees who work on a three-shift, 24 hr/day, ~350 day/yr schedule. The production rate is ~400 t/day, and once or twice per year brief maintenance periods are taken (Frei, 1999).

Summary

Table 4.3 lists some of the companies that have produced sodium sulfate in the United States, noting the period of operation and the purity of their product, if available.



Figure 4.37 Storage and truck loading facilities at Cedar Lake, Texas. (Courtesy of Cooper Natural Resources.)

Table 4.3

Some of the Companies That Have Produced Sodium Sulfate in the United States

Location/Company	Date operated (purity, %)	Tonnage, short tons
<i>Arizona: Mesa Verde</i>		
Unknown companies	Intermittently since 1890	Very small
Western Chemical Co.	1920–1926 (95+)	80–120 t/day
Arizona Chemical Co.	1930–1933 (95.1)	3000 t/mo
<i>California</i>		
<i>Bertram (Durmid Hills; Imperial Valley)</i>		
E.H. Otto & Company	Nov. 1922–June 1923	2500 t
American Sulfate Co.	Jan. 1940 (4% MgSO ₄)	250 t
<i>Dale Lake</i>		
Unknown companies	Intermittently “very early”	Very small
Unknown company	Late 1950s; winter spray	Small
Dale Chemical Industries	~1952 for 6 mo.	100 t/day
<i>Danby Lake</i>		
Unknown company	Mid-1960s	Very small
<i>Searles Lake</i>		
American Potash & Chemical Co.	1934–1967 (98+)	45–250 kt/yr
Stauffer Chemical Co.	1958–1970 (99+)	100–150 kt/yr
Kerr-McGee Chemical Co.	1967–1990	250–475 kt/yr
North American Chemical Co.	1990–1998	250–220 kt/yr
IMC Global	1998–Present	220 kt/yr
<i>Soda Lake (Carriso Plain)</i>		
Carisa Chemical Co.	1908–1915 (intermittent)	Small
Unknown company	1963 (91.6%)	Small
<i>Montana: Westby Lake</i>		
Unknown company	1952	Small
<i>Nevada</i>		
<i>Rhodes Marsh</i>		
Rhodes Alkali & Chemical Corp.	1930–1932 (97.3%)	50 t/day (20,000 t total)
<i>Wabuska</i>		
American Sodium Co.	1930	1000 t
<i>New Mexico</i>		
<i>White Sands Deposit</i>		
Southern Chemical Co.	1919	Pilot plant
<i>Dona Ana County Brine</i>		
Ozark Mahoning Co.	1951–1957	Brine shipped to Monahans, Texas (modest amounts)
<i>North Dakota</i>		
<i>Grenora #2</i>		
Ozark-Mahoning Co.	1977, 1984	Development studies

(continues)

Table 4.3
(continued)

Location/Company	Date operated (purity, %)	Tonnage, short tons
<i>Stanley 1, 2, A</i> American Colloid Co.	1961–1964	Large pilot plant
<i>Texas</i>		
<i>Soda Lake (Monahans)</i> Ozark-Mahoning Co.	1933–1970	40,000 t/yr (>1,000,000 t total)
<i>Brownsfield Lake</i> Ozark-Mahoning Co.	1955 (?)–1987	35,000–70,000 t/yr
<i>Rich Lake</i>	?–1987	Part of above
<i>Mound Lake</i>	1981–1987	Part of above
<i>Cedar Lake (Seagraves)</i> Ozark-Mahoning Co.	1968 (?)–1992	95,000–150,000 t/yr
Elf Atochem	1992–1996	150,000 t/yr
Cooper Natural Resources	1996–present	150,000–165,000 t/yr
<i>Utah: Great Salt Lake</i>		
Midwest Dye & Chemical	Intermittent to 1920	Very small
Minerals Salt Co.	1920	Small
Salt Lake Sodium Products Co.	1934–1939	Large pilot plant
Same	1939–1940 (97.9%)	25 t/day
Great Salt Lake Minerals	1976–1989	35,000–50,000 t/yr
North American Chemical Co.	1989–1993	50,000 t/yr
<i>Washington</i>		
<i>Sulfate Lake</i> Paul Donaldson	1916–1917	2500 t
<i>Virginia Lake</i> Naso Chemical Co.	Early 1930s	Very small
<i>Lawson Lake</i> Washington Chemical & Salt Co.	1942–1943	100 t/day plant; no product
<i>Cameron, Morris, Penley Lakes</i> Okanogan Salt Co.	1950	Very small
<i>Huan Lake</i> Weltha Chemical Processing Co.	1958	Very small
<i>Wyoming</i>		
<i>Union Pacific Lakes</i> Laramie Chemical Works	1885–1892 (96.4%)	~10 t/day glauber salt
<i>Sodium Lake</i> Gill Soda Co.	~1920–1926 (?)	Small
Columbian Hog&Cattle Powder Co.	~1926–<1935	Small
<i>Bull Lake</i> Iowa Soda Products Co.	1928–>1960 (96%)	2000–6000 t/yr (100,000 t total)
<i>Gill Lakes</i> Pratt Sodium Sulfate Co.	1930 (?)–>1960	2000 t/yr

GENERAL PROCESSING STUDIES

Glauber Salt Crystallization

Many studies have been made on the crystallization of glauber salt, from the point of view both of the equipment or procedures involved and of its more theoretical aspects. The equipment used by various natural sodium sulfate producers, as discussed in the previous section, varies widely from air-cooled ponds (as have been used in Canada, Turkey, etc.), spray pipes (Searles and Dale Lakes), or spray towers (Canada and Spain); to a coolant in polished tubes within agitated tanks (West End, Searles Lake); to scraped-surface coolers (Texas); to multicompartiment (Lurgi-type) vacuum crystallizers (Spain); to conventional or growth-controlled vacuum or heat exchange crystallizers (many companies). Neville (1987) outlined some of the important considerations in selecting glauber salt crystallization equipment, and suggested a flow sheet for the cooling tower–crystallization process (Fig. 4.38). With it, impure strong-sodium-sulfate brine from solar ponds, or impure and/or weak leach brine from ore deposits, would first be settled and, if required, filtered. It would then be heat exchanged with depleted brine that was being returned to the solar ponds or the deposit, and the cooled brine would be sprayed into a cooling-tower-type crystallizer. Using air as the cooling medium, as with some other types of crystallization equipment, would be relatively inexpensive in initial and utility costs, but the production throughout the year would be highly variable, and the recycle load would be very high because of the poor cooling that usually would be obtained. Also, here as with most of the novel crystallizing methods, the glauber salt particle size would be fairly small and variable, resulting in more entrained brine in the glauber salt, and thus lower product purity and a greater evaporation expense.

Many other suggestions for less conventional glauber salt crystallizing equipment have been made, such as the concept of Matynia *et al.* (1989) of using jet pumps for more gentle slurry circulation than conventional pumps. With a classified growth-controlled crystallizer they obtained an average glauber salt crystal size of 12–16 mesh with a coefficient of variation of 20–30%, and a mean volume shape factor of 0.64–0.66. The crystal size varied with the crystal residence time (τ) over the range of 0.56–1.25 hr and slurry densities of 4–25 wt% as $L = 0.05\tau^{0.39}$. Similar results might have been expected with the modern mixed or parallel flow circulating pumps and the same growth-controlled crystallizer. Examples of other articles on glauber salt crystallization equipment include those by Ando *et al.* (1969), Belomytsev *et al.* (1993), Chilton (1958), and Winkler (1973).

There are also some articles on the kinetic factors in glauber salt crystallization, such as that by Graber *et al.* (1996). In a study of three different small (1.8–13.8 liter), jacket-cooled, agitated-tank continuous crystallizers with normal slurry density (not thickened) and no fines removal, the nucleation rate was $B = 2.75 \times G \times Mt^{0.5} \times N^{1.9} \times D^{0.7}$, where G is the growth rate, Mt the suspension density, N the agitation rate, and D the impeller diameter. They found no effect on the particle size or uniformity with crystal residence times in the range of 35–45 min, except that at

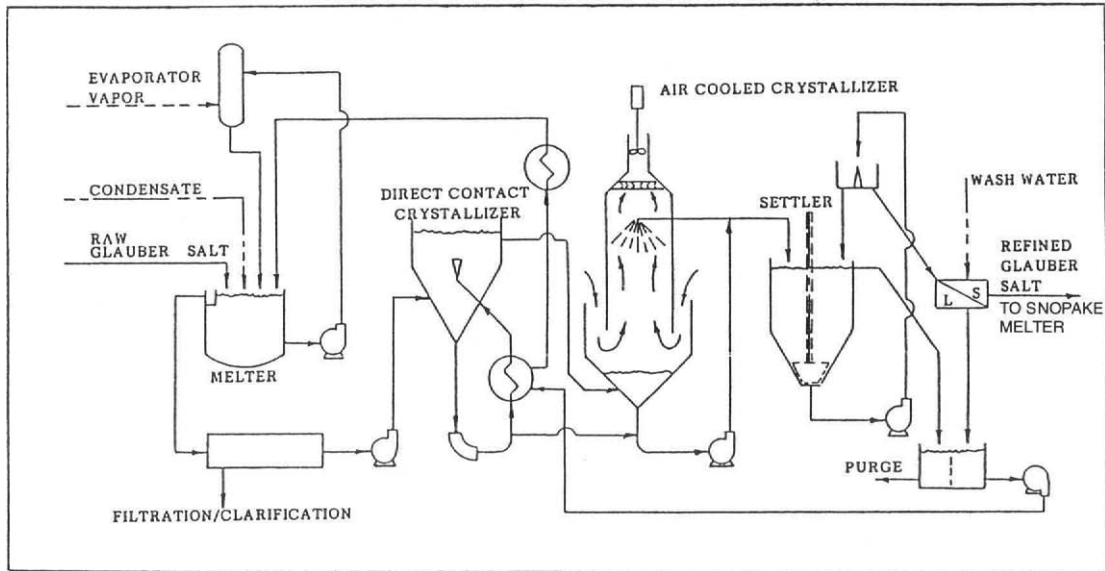


Figure 4.38 Spray cooling process for dissolved crude glauher salt. (From Neville, 1987, courtesy of Whiting Equipment Canada, Inc.)

the longer times the crystal breakage and rounding effect began to be counterproductive. The crystallizer size and the operating temperature (between 16 and 20°C) had no effect on the operation. The form factor (inverse fraction of its longest dimension compared to a cube with the same volume) for the decahydrate was 0.55. Other articles on the theory or kinetics of glauber salt crystallization include those by Bentwoglia (1927), Edle *et al.* (1983), Krichevskaya (1945), Pokhodenko *et al.* (1974), Prokhorenko *et al.* (1980), Sedelnikov *et al.* (1973), Skrivanek *et al.* (1975), Stockerl and Kohler (1991), and Taboada and Graber (1991). In a very different type of study, Knacke and VonErdberg (1975) noted that anhydrous sodium sulfate expands ~300% as it converts to mirabilite, and that attempting to restrain the hydration process can reach pressures of 200 kPa/cm².

Evaporation: Crystallization of Anhydrous Sodium Sulfate

To produce a relatively pure anhydrous sodium sulfate product in industrial equipment, the feed material (brine or glauber salt) must contain the minimum amount of insoluble material and be as free as possible of other soluble salts. This may require purifying the dissolved glauber salt or feed brine (and perhaps filtering it), and if glauber salt is to be produced in an intermediate step, dewatering it effectively and perhaps washing the crystals. The brine or glauber salt evaporators then must have a high capacity to reduce the unit costs, must have a low operating and maintenance cost, and must be thermally efficient. This requires that low value or waste heat be utilized for melting the glauber salt, and that a multiple effect or vapor-recompression evaporator be employed. A fines removal system or a growth-controlled unit would also produce a more pure, uniform, coarse and higher-quality product. Finally, a bleed stream should be removed if there is a substantial amount of other salts present.

Several articles, such as that by Neville (1987), discuss the factors involved in the selection of conventional multiple effect (Fig. 4.39 to 4.41) or vapor recompression evaporators (Fig. 4.42). He noted that the heat required to melt glauber salt is high (244.2 kJ/kg), and that with multiple effect units the melting can be economically done by steam (the evaporated water) from the last effect. This low-value heat eliminates the energy required to otherwise melt the glauber salt, saves on the cooling water required to condense these vapors, and increases the thermal efficiency of the unit compared to recompression. However, if waste heat from other sources is available (such as from condensate, glauber salt crystallizer's barometric condensers, or direct contact with flue gas) then vapor recompression is usually the more efficient evaporation method.

With sodium sulfate's inverse solubility at higher temperatures, the lowest solubility is at the first (hottest) effect, making that a good place to remove a bleed stream if there are considerable impurities in the brine or glauber salt, and the feed and centrate enters all of the effects equally. However, with the normal low-impurity

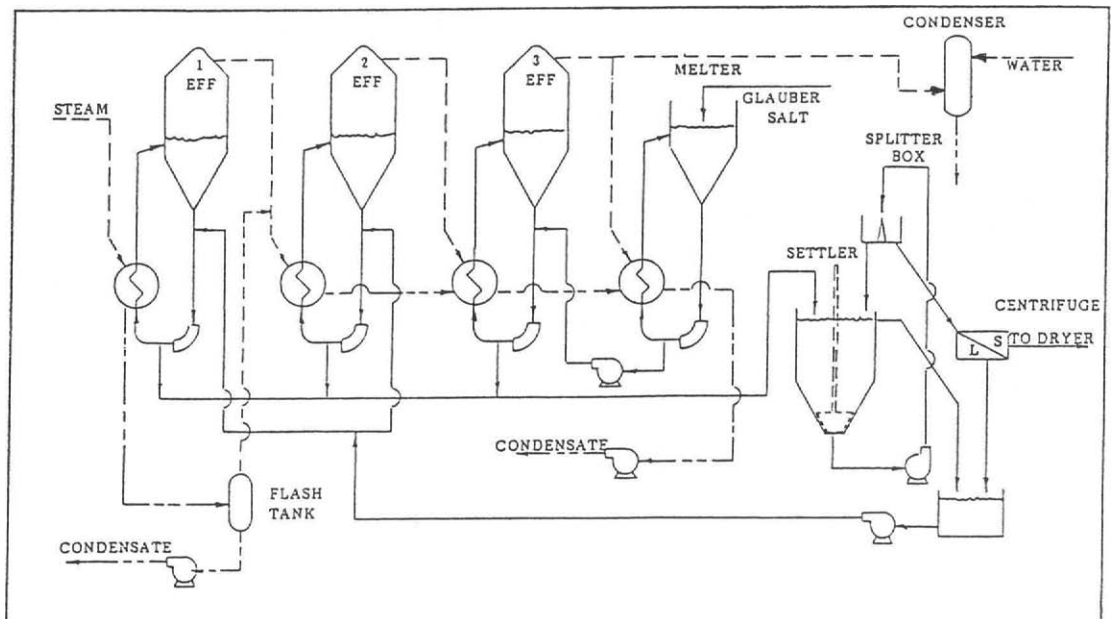


Figure 4.39 A typical glauber salt evaporator (with feed to the third effect). (From Neville, 1987, courtesy of Whiting Equipment Canada, Inc.)

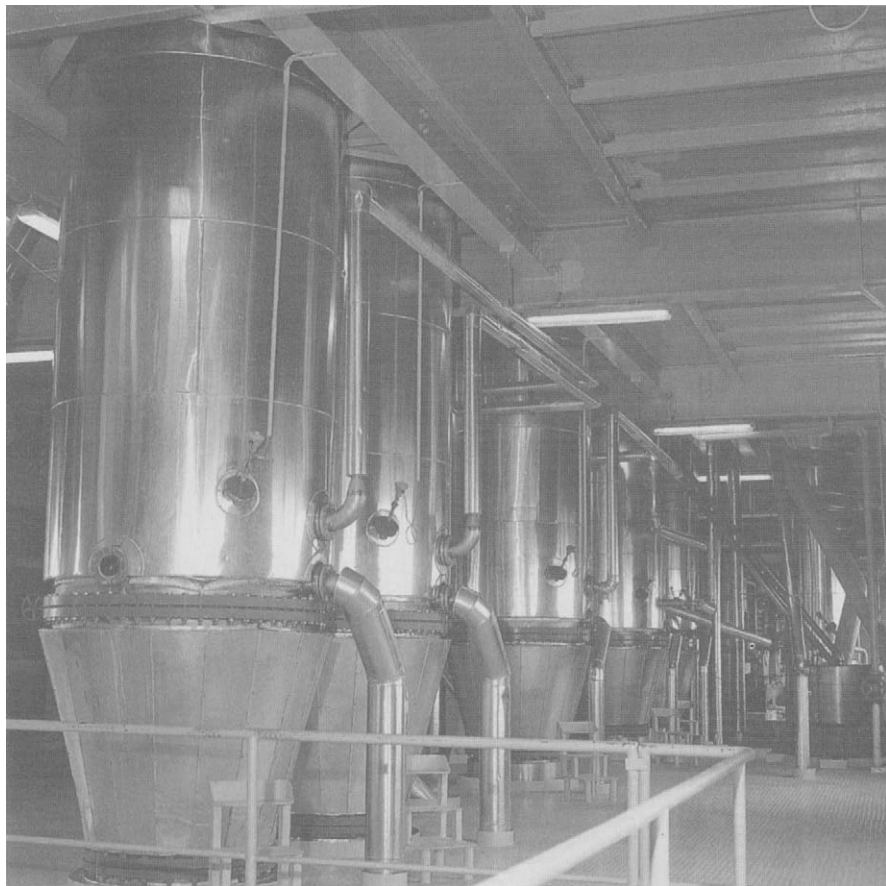


Figure 4.40 Small multiple effect evaporator bodies for sodium sulfate. (Courtesy of Alkim Alkali Kimya Anonim Sirketi.)

mirabilite, or if the feed enters at the last effect and centrate is returned to the first and second effects (and product taken from all the effects), the impurities would concentrate and a second effect bleed would result in the lowest sulfate loss. To produce the largest and most uniform crystals a fines-destruction system should be employed, such as by classifying the centrate and adding water to the stream with the finest crystals (to dissolve them). The normal design of high velocity through the heater tubes, a low ΔT through and across the tubes, and a high slurry density within the unit (~ 25 wt%) is also required to minimize tube and body fouling and grow better crystals. Under these conditions washout periods of 2–4 weeks should be realized, with the vapor recompression units usually requiring fewer washouts. Effective vapor demisters and provisions for adding an antifoamant to the bodies



Figure 4.41 Circulating pumps from evaporator bodies to heaters. (Courtesy of Alkim Alkali Kimya Anonim Sirketi.)

should be made, especially with recompression and if the glauber salt was crystallized from a high-organic brine.

In previous years and for smaller plants or special circumstances, a wide variety of other crystallizers and evaporators have been proposed, and two that at one time had a wide acceptance are discussed below.

Submerged Combustion

In western Texas and Canada, natural gas has been quite inexpensive, and in the early days of the industry smaller plants and less demanding product quality allowed submerged combustion evaporators (Fig. 4.6) to be popular. They were developed at a time when conventional evaporators often had severe scaling problems, so equipment that was slow to become fouled and had a low capital cost was more important than poor fuel efficiency and product crystal size. A simple large-diameter steel tube was used as the burner, and a mixture of gas and air was ignited by an incandescent wire near the base of a conical-bottom stainless steel tank. The flue gas vigorously agitated the melted mirabilite in the tank, evaporating its water and crystallizing anhydrous sodium sulfate. The burner was usually a 30-cm (12-in) pipe, 1.1-m (44 in) long (with a 0.19 m^3 [2 ft^3] volume), and reduced to 13 cm (5 in) at its upper piping connection (if it were any smaller, scale buildup and bridging soon plugged the tip and put out the flame). It could deliver 139,000 Btu/min, had flame

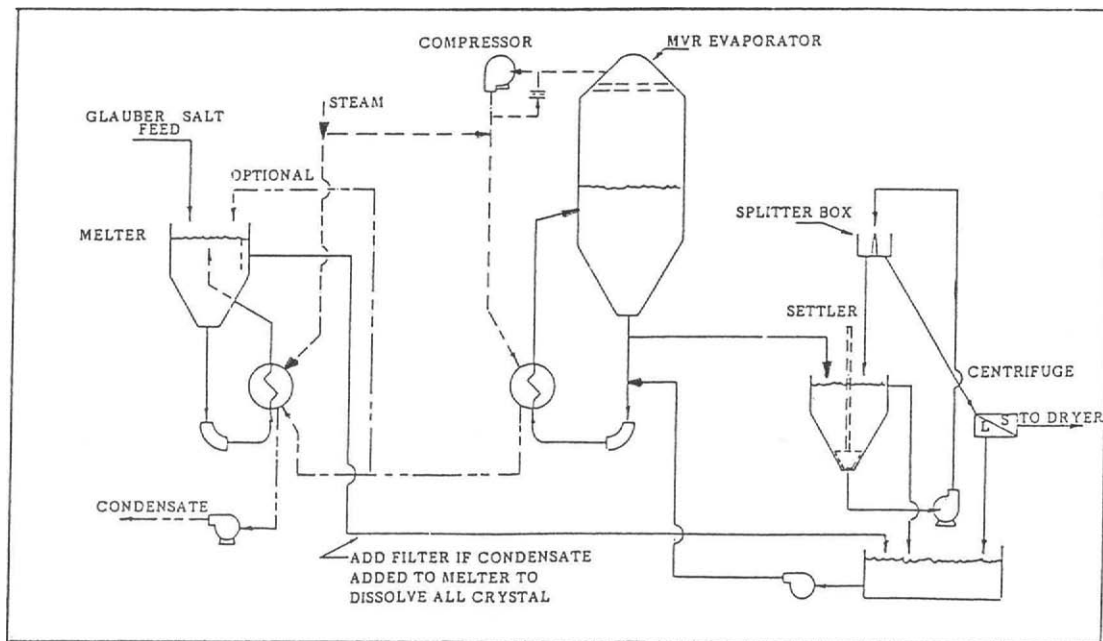


Figure 4.42 A typical vapor recompression glauber salt evaporator (with partial melting by condensate). (From Neville, 1987, courtesy of Whiting Equipment Canada.)

temperatures of up to 1316–1538°C (2400–2800°F), and made the brine temperature about 88°C (190°F) with a nearly 90% fuel efficiency. The burner wore out by scale popping off and taking some steel with it after the production of about 500 t of sodium sulfate. The evaporator tank was usually 2.4 m (8 ft) in diameter and 3.6 m (12 ft) in height.

At Ozark-Mahoning's Monahans, Texas, plant a 5% slurry of sodium sulfate was maintained in the evaporator, with some continuously withdrawn and initially sent to a 1.5-m diameter by 3-m high settler. Its 70% solids underflow-slurry went to either a centrifuge and then a 0.9-m diameter, 7.5-m long dryer (to produce a >99% Na₂SO₄ product), or directly to a 2.1-m diameter, 18-m long dryer to produce a less pure product. The settler's overflow brine and the centrate were partly used to re-pulp and melt the entering mirabilite, and partly returned to the evaporator (less a small bleed stream; Douglass and Anderson, 1941; also see the Texas and Canada sections). Other articles on submerged combustion include those by Anon. (1953) and Kobe *et al.* (1936).

Spray Evaporators

Many designs of spray evaporators have been suggested for the production of anhydrous sodium sulfate, and one, the *Holland Evaporator* (Fig. 4.5), has seen widespread industrial use in the early period of operation in Canada. Spray-column brine preheaters or glauber salt melters have also been employed using the waste heat from flue gas passing through sprayed or splashed brine or mirabilite melt liquor. A description of the Holland evaporator has been given in the section on Canada (Chaplin Lake, Saskatchewan Minerals), but basically it was a unit that splashed melted glauber salt slurry into a flue gas stream and removed anhydrous sodium sulfate from its base by a drag conveyor (Holland, 1951). Other examples of this type of evaporator have been given by Schultz and Lavine (1942), who proposed using a standard spray column with the flue gas supplied by the plentiful lignite of the Canadian and North Dakota plains. Comings and Coldren (1957) and McLain *et al.* (1957) proposed using a flash-evaporator, where the melt would be atomized into a high-velocity flue gas stream. Bakhshi and Nihalani (1974) and Bakhshi and Chai (1969) proposed injecting the mirabilite melt into a flue gas-heated fluidized bed that was filled with closely sized sodium sulfate, constantly withdrawing a product stream and adding more sized sodium sulfate if necessary to maintain the bed. There are a large number of other articles and patents on this type of equipment, as indicated by a few examples listed in the Reference section.

Theoretical

Several studies on the kinetics of anhydrous sodium sulfate crystallization have been reported, such as the articles by Graber *et al.* (1996) and Gurato *et al.* (1984), they also discuss the effect of impurities on the crystallization). Klug (1985) and Klug and Pigford (1989) indicated that individual crystals have a constant growth

rate that is dependent upon the temperature but not the supersaturation conditions, and that other crystals (i.e., impurities) in the same environment have a range of growth rates. In single crystal experiments at 60–69°C with 0.1–0.2% levels of supersaturation (the actual concentration minus the saturated concentration/saturated concentration), the Na_2SO_4 crystals grew in a dipyramidal habit composed of eight equal [111] faces. In a batch agitated crystallizer there was less spread in the particle sizes when the solution was seeded, and the crystal growth rate was faster. In this unit the size dispersion increased with prolonged crystal residence times. Gaglia *et al.* (1984) have studied the range of metastable limits in the crystallization of anhydrous sodium sulfate.

Centrifuging (or Filtering), Drying, and Granulation

The centrifuges or filters used to dewater both glauber salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and anhydrous sodium sulfate slurries should reduce the moisture content of the cakes to the lowest economic level, and allow some crystal-washing if desired. Centrifuges usually reduce the moisture content of the cake to a lower level than filters, with common values being pusher centrifuges 4–6%, screen or solid bowl centrifuges 5–8%, and filters 8–12%. Filters can handle smaller particles, solid bowls next, and pusher or screen bowl units require a larger particle size. Each of the centrifuges allows more solids to escape in the centrate than filters, whereas screen and solid bowl centrifuges have a higher capacity than the other units. Filters (especially belt filters) allow the easiest and most complete cake washing.

Sodium sulfate dryers should be capable of reducing the moisture content to a low level to minimize future product caking, and should also be followed by screening, dust removal, and often product cooling. Both rotary and fluidized bed dryers can be employed, with the latter usually having an integral cooling, air preheating section. Rotary dryers are often fired in a counterflow manner in order to provide the maximum moisture removal, but then product coolers are usually required. In the subsequent screening section the fines are often discarded or reprocessed because of their lower purity and particle size, and the oversized particles are crushed and returned to the screens. There is a more limited literature on centrifuging, drying, and the other unit operations involved in sodium sulfate processing, but a few typical examples are in the Reference list.

Salting Out with Sodium Chloride or Methanol

The solubility of sodium sulfate is so much less in solutions saturated with sodium chloride than in pure water that the addition of NaCl to glauber salt or sodium sulfate solutions to precipitate anhydrous Na_2SO_4 , or decrease its solubility, has become a commonly considered processing method, and several companies have used it for large-scale commercial production (see the Searles Lake, Texas, and Chilean nitrate

sections). The disadvantage of the procedure is that any insolubles with the salt or glauber salt may remain with the product, and the sodium sulfate particle size is often small and variable.

A number of authors have also suggested the use of methanol (CH_3OH) as a salting-out agent. For instance, Fernandez-Lozano (1996) showed that forming a 60 wt% methanol solution with low-density sea water bittern (containing 6% Na_2SO_4) could precipitate up to 94% of the sodium sulfate as a 60% Na_2SO_4 intermediate product. It could then be leached by a 50% methanol solution to produce 97.8% Na_2SO_4 , 1.5% MgSO_4 , 0.4% K_2SO_4 , and 0.3% NaCl . Unfortunately, the cost of the equipment and lost methanol, and of removing the bulk of the methanol from the reject bitterns by distillation and steam stripping would be very high. Several other articles suggesting this process are listed in the Reference section.

Solar Ponds and Air Spraying

One of the common processing techniques in the production of sodium sulfate is the use of solar ponds (Figs. 4.1, 4.43–45) or air spraying. Both methods can be used for the crystallization of glauber salt by natural cooling, as well as the concentration of dilute brines. Solar ponds can also be used to form anhydrous sodium sulfate by evaporation at higher temperatures, or the dehydration and drying of glauber salt. The air spraying of brine to produce glauber salt can be accomplished either in ponds or on a playa (Fig. 3.40), or in crystallizing towers in the plant (Fig. 4.38). Brine can also be sprayed into flue gas for heating, or evaporation to form anhydrous sodium sulfate (Fig. 4.5). Each of these procedures has been commercially employed (as noted in the earlier sections), and various references on the subject are given in the Reference list.

Glauberite Processing

Because of glauberite's ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$) occurrence in large, fairly pure deposits that occasionally are easy to mine (Fig. 4.46) or prepare for *in-situ* leaching, and its high solubility, it has become a major sodium sulfate raw material (see the Spanish, Mexican, Former Soviet Union, and Turkish processing sections). Plantalamor Rovira (1981) noted that the leaching operation is exothermic, that the residual gypsum weighs 61% as much as the original glauberite, and that the residual volume of the gypsum is 86% of that of the glauberite. Most of the early patents on glauberite processing discussed the formation of *in-situ* leaching pits and of the means of circulating brine through them (e.g., Plantalamor Rovira, 1981; Minerresa, 1981). Later patents considered the concept of leaching the glauberite at a low temperature (15–32.4°C) and with limited water in order to form a slurry of glauber salt with the residual gypsum (instead of merely dissolving the sodium sulfate). Then additional water would be added if needed, and the temperature raised above the glauber salt transition

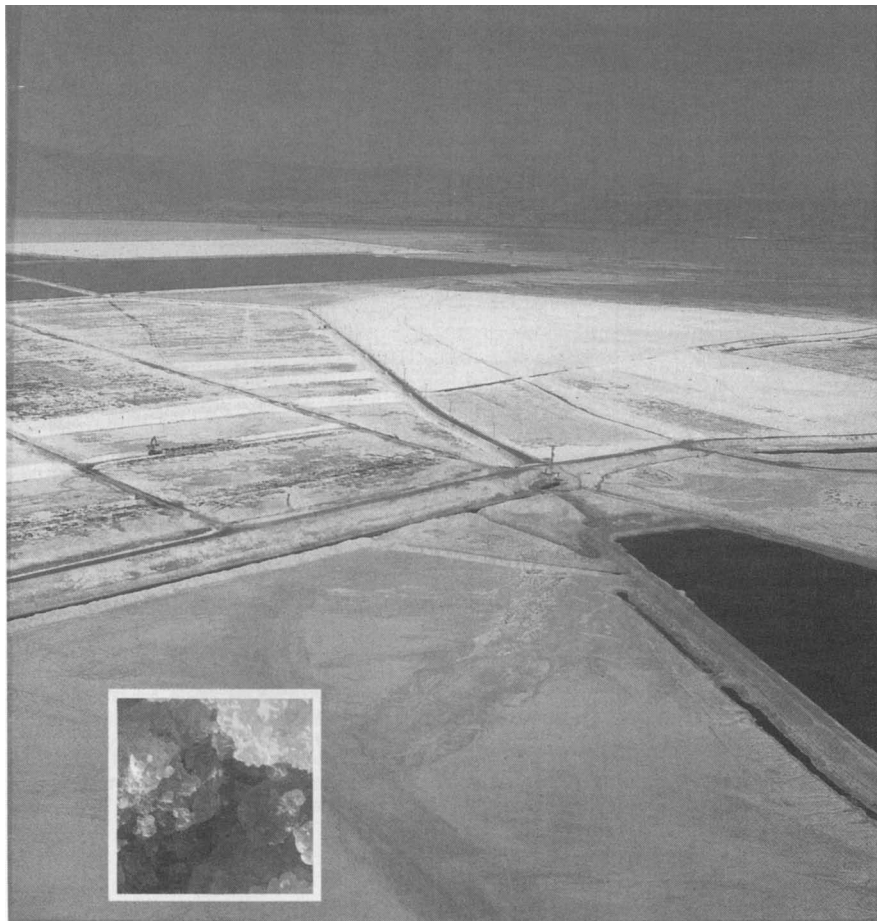


Figure 4.43 Brine evaporation/cooling ponds at Acigol Lake, Turkey. Insert: glauber salt crystals. (Courtesy of Alkim Alkali Kimya Anonim Sirketi.)

temperature (32.4–100°C) so that the glauber salt dissolved. In this manner the concentration of the leach liquor could be raised from about 140–240 g/liter to 300–420 g/liter, depending on the degree of leaching, conversion, and the presence of other salts (Lluís Pellisa and Plaja Tarres, 1993; Wang and Lu, 1990; Dean and Posego, 1974). Guo *et al.* (1993) investigated the kinetics of leaching different glauberite ore particle sizes, solution temperatures, and concentrations, and other variables including methods of reducing the concentration of calcium sulfate in the leach solutions. They also determined the heat of solution of glauberite to be 50.54 kcal/mol. Li (1993) studied methods of purifying the leached glauberite solution. Freyer *et al.* (1997) studied some of the phase chemistry of the sodium–calcium sulfate series $\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$



Figure 4.44 Brine inlet canal and pumping station at Acigol Lake, Turkey. (Courtesy of Alkim Alkali Kimya Anonim Sirketi.)

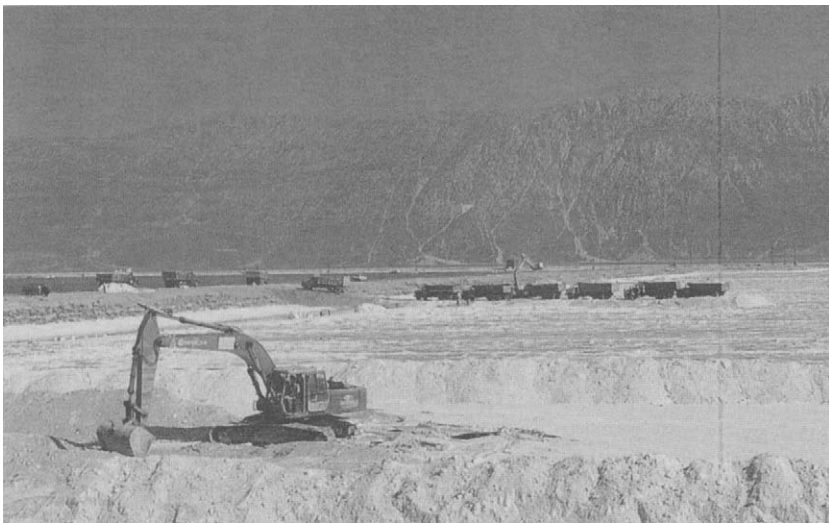


Figure 4.45 Glauber salt harvesting at Acigol Lake, Turkey. (Courtesy of Alkim Alkali Kimya Anonim Sirketi.)



Figure 4.46 The mining of clear crystalline glauberite in Turkey. (Courtesy of Alkim Alkali Kimya Anonim Sirketi.)

(glauberite), $2\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$ (metastable glauberite), $2\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (labile glauberite), and $5\text{Na}_2\text{SO}_4 \cdot 3\text{CaSO}_4 \cdot 6\text{H}_2\text{O}$ (hydroglauberite). Various authors have proposed methods of producing other salts from glauberite, such as potassium sulfate by Yunusova *et al.* (1990) and Yanateva *et al.* (1979), and sodium nitrate by Wang *et al.* (1997b). Various other literature sources on glauberite processing are given in the Reference list.

Astrakanite and Burkeite Processing

It has often been considered that sodium sulfate should be readily obtainable from its double salts by the correct manipulation of their four component phase systems. The reciprocal salt pair $\text{Na-Mg-SO}_4\text{-Cl}$ has thus been extensively studied, by Artykova *et al.* (1985) and many others. Astrakanite ($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$) occurs in some large deposits, and may also be formed from single salts such as epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and halite (NaCl ; as can be crystallized after the salt-producing period in commercial sea water solar salt ponds, or end liquor from potash plants). These salts can be dissolved and evaporated (in solar ponds or elsewhere) to produce the astrakanite. The simplest processing method for astrakanite involves first converting it to vanthoffite ($3\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4$) at higher temperatures ($80\text{--}100^\circ\text{C}$), and then partially leaching it, or reacting it with NaCl (at $80\text{--}100^\circ\text{C}$), to produce anhydrous sodium sulfate. The residual brine may then be cooled and/or evaporated to recycle mirabilite and/or produce MgCl_2 and/or MgSO_4 if desired. Haucuz and Silis (1992) have proposed using the process in solar ponds, utilizing the hot NaCl brine generated by three separate and adjacent salt-gradient ponds. However, even though in general these reactions do work, a great deal of heating, cooling and evaporation are required. Also, the reactions' approach to equilibrium, the reaction rate, the uniformity of the reaction, and the yields are not nearly as good as for the comparable reactions producing potassium sulfate. In laboratory and pilot plant tests the control of the operations has been found to be much more difficult, and the product purity often quite poor (Garrett, 1965). However, a somewhat similar process utilizing an astrakanite-halite mixture is employed by Soquimich in Chile. The mixture acts as a dissolving reaction, but mainly a salting-out agent for glauber salt, thus recovering some of the sodium sulfate from the astrakanite (see the Chilean nitrate section).

Another sodium sulfate double salt, burkeite ($2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$), has had its sodium sulfate content recovered in a large commercial plant at Searles Lake, California, by the metastable salting-out of a burkeite solution with salt from the plant evaporators. Also, burkeite was used at that location in the formation of potassium sulfate (see the Uses chapter). Burkeite is used in some detergent formulations, and burkeite is deposited as a scale-forming compound in kraft pulp and paper making. For these reasons there is considerable literature on burkeite listed in the Uses chapter, and others in the Reference section.

Forming Other Salts From Sodium Sulfate

Potassium Sulfate

One of the principal methods of producing potassium sulfate (a large-tonnage fertilizer) is by the reaction of potassium chloride (potash) with sodium sulfate to first form glaserite ($3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$) as an intermediate product. The general technology and commercial application of this process are discussed in the Uses chapter, but some of the secondary and related references on the production of potassium sulfate from sodium sulfate or its compounds are listed below.

Other Products from Sodium Sulfate

Suggestions have been made to produce many other compounds from sodium sulfate or its ores, as indicated by several examples in the Reference list. Some of the commercial applications have been listed in the Uses chapter, but as far as is known, none of the other process suggestions have been commercialized.

Recovering Sodium Sulfate from Wastes or Other Solutions

There are a very large number of articles on processes for obtaining glauber salt (or sodium sulfate) from waste or nonore solutions. Most of this literature is concerned with special sodium sulfate sources, such as where sodium sulfate is desired to be removed or recovered as a by-product from the production of other chemicals, wastewater, or liquors (such as salvaged battery acid). This voluminous literature is beyond the scope of this book, and in fact, constitutes the subject of “synthetic or by-product” (and not “natural”) sodium sulfate. However, a few of these articles on sodium sulfate recovery are given in the Reference list to provide a brief look at the subject.

General Processing: Other Countries, Other Technology

There are many articles on the general processing of sodium sulfate, or on processes involving sodium sulfate or its ores, that are not covered in the preceding sections. Some of this literature is listed in the Reference section.

ENVIRONMENTAL CONSIDERATIONS

Sodium sulfate and its mineral compounds are quite harmless and environmentally friendly substances. Except in very large amounts they have essentially no toxic effect to humans, animals, or plants, and small amounts are beneficial to the growth of each of them. Sodium sulfate has been used as a salt substitute for human and animal food, and the sulfate ion and to a lesser extent sodium are essential plant

nutrients. Sax (1979) states that "the toxic qualities of . . . the sulfate (ion) is that of its . . . cation," and each of its common forms, with sodium, calcium, magnesium, or potassium, is thus relatively inert and harmless. It is this quality of environmental friendliness that has contributed to its usefulness in detergent formulations, as well as in carpet cleaners, dyeing, and similar applications.

Its specific toxicity ratings are as follows: The LD₅₀ (mouse) is 5989 mg/kg (the dose at which half of the mice eating it die; by contrast, ordinary table salt has an LD₅₀ (rat) of 3000 mg/kg, or in other words is roughly twice as toxic). The intravenous LD₅₀ (rabbit) is 1220 mg/kg, which is the same as the lowest reported value for mice (LD_{Lo} [mouse]). It is not a carcinogen and has no reproductive or tumorigenic effect, making it classified as being "slightly toxic by ingestion," and larger doses usually act as a purgative.

The suggested nuisance dust limits are 5 mg/m³ as respirable (very fine particle) dust; the total dust level should be limited to 10 mg/m³ (ACGIH TWA) or 15 mg/m³ (OSHA TWA; these are the two agencies' general nontoxic dust recommendations). A study of 119 workers exposed to sodium sulfate dust, some for 10 years, showed no abnormalities of pulmonary function or other aspects of health. However, laboratory epidemiologic studies have shown an excess risk of asthmatic attacks in the general population to be correlated with elevated levels of suspended sulfate particles in the air. It may also cause minor skin irritation upon prolonged exposure. Simple dust masks and face shields or safety glasses (it may cause some eye irritation) are recommended when working in a very dusty environment. Sodium sulfate poses no fire or reactivity hazards and is considered nonhazardous when transported (CGD UK; Fisher, 1996; Ox.Ac.UK, 2000). Several other references on its environmental properties are listed below.

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Sodium sulfate is a large tonnage industrial chemical that is often called “salt cake” based upon its former “synthetic” source of reacting salt with sulfuric acid. As would be expected, it has a very large number of uses, but as has happened before, this usage pattern has changed dramatically since the early to mid-1970s (Table 5.1 and Fig. 5.1). Before that time by far the greatest single use of sodium sulfate was as the principal wood delignification raw material in the production of kraft paper, representing 70–75% of the total salt cake consumption. The kraft process is the world’s major pulping method, being used for 83% of the U.S. pulp market in 1990 (120 mills), and it had been an even higher percentage of pulp production before that date. However, in the 1970s environmental pressures began to require almost total recycling of the chemicals in the spent digestion liquors (Anon., 1983), and to a lesser extent there developed competitive pulping processes, alternative sources of sulfur, and by-product sodium sulfate generation from chlorine dioxide pulp bleaching. Consequently, by the late 1990s this usage had dropped to a fraction of its former amount, becoming only 12–13% of the total U.S. sodium sulfate consumption. Only 12 U.S. kraft mills were still purchasing sodium sulfate in 1994 (Anon., 1999–1965).

Fortunately, in the intervening years the use of sodium sulfate as a detergent filler had increased, rising since the mid-1970s to 40–60% of the total sodium sulfate consumption in the 1990s. Various of the other uses have also remained nearly constant or slightly increased (Kostic, 1999–1979). The net result of these marketing changes has been a steady decline in United States’ sodium sulfate consumption and production, and a corresponding increase in the purity and quality of the product. A fairly crude product was initially (and in isolated cases still is) acceptable as a pulping reagent and for some other uses, but the detergent filler must be pure, very white, and closely sized. This in turn has had a major influence on the manufacturing processes and greatly increased the product’s average price. Several of these major sodium sulfate uses will be described in more detail in the following sections.

Table 5.1
U.S. Sodium Sulfate Sales Pattern, % of Total Consumed^a

Year	Detergents	Textiles	Kraft paper	Glass	Misc.
1998	45	18	13	10	14
1997	42	15	12	11	20
1996	43	15	12	11	19
1995	49	18	13	10	10
1993 ^b	40	17	27	7	9
1992 ^b	44	18	28	8	2
1991 ^b	51	—	26	5	18
1990 ^b	60	—	28	4	8
1989	57	10	27	4	2
1988 ^b	52	—	30	6	12
1987 ^b	50	7	30	6	7
1986 ^b	48	6	27	6	13
1985 ^b	38	—	54	6	2
1984 ^b	43	5	42	5	5
1983 ^b	43	—	47	5	5
1982 ^b	40	—	46	5	9
1981 ^b	39	3	48	8	2
1980 ^b	39	2	48	6	5
1978	40	—	45	11	4
1975	20	—	70	—	10
1973	21	—	64	11	4
1972	19	—	66	12	3
1971	17	—	67	12	4
1968	12	3	70	10	5
1965	10	—	70	8	12
1964	7	3	71	11	8
1959	7	3	71	11	8
1954	16	—	74	—	10
1951	5	4	75	8	8

^aAnon., 1999–1965; Kostic, 1998–1979; Anon., 1971–1961.

^bKostic data used as is, or averaged for the years noted.

DETERGENTS

Sodium sulfate is used as a filler or substrate in many powdered, granular, or solid detergent formulations. In North America (Canada, the United States, and Mexico) the average box of laundry detergent in the 1990s contained 20–25% sodium sulfate, and some formulas contained up to 50%. It is an excellent diluent and standardizing material, providing good flow properties and slightly enhancing the detergent efficiency by stabilizing the colloidal properties of the removed “dirt or soil.” It also reduces the critical micelle concentration of the organic surfactant, lowering the strength at which good washing can be achieved. It is easily processed, neutral, compatible with all of the other detergent ingredients, noncorrosive, nearly inert,

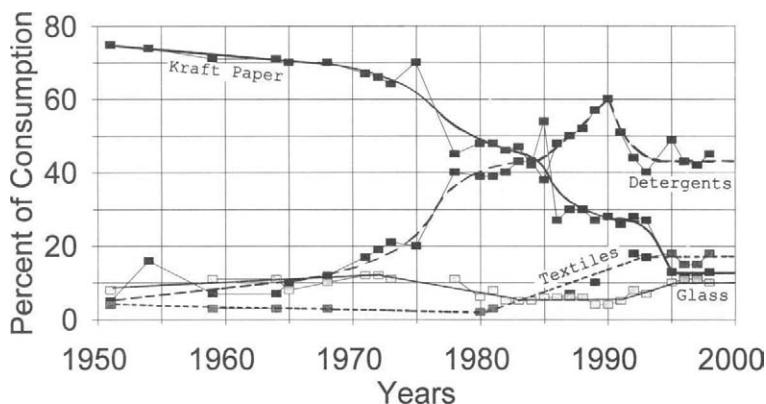


Figure 5.1 U.S. sodium sulfate use pattern, % of total consumption. (From Anon., 1999–1965, 1971–1961; Kostic, 1999–1979.)

nontoxic and not environmentally objectionable. It can be very pure and white to help make the detergent more attractive, and also can be produced in the desired uniform particle size to mix well with the other materials and/or be dissolved and easily spray dried as a supporting agent. Its one drawback is that it may slightly aid in the redeposition of the removed soil, which somewhat reduces its net contribution to the washing efficiency.

The major use of sodium sulfate in this application depends upon the “big box” powdered detergent market, and this form of cleaning agent sales has many competitors. Liquid detergents, high-strength (“superconcentrates”) and/or measured dose briquets, and many special formulations (such as with oxidizers or enzymes) have been increasing in popularity and use little or no sodium sulfate. However, there has also been some reformulation to tetrasodium pyrophosphate instead of sodium tripolyphosphate (STPP) in order to reduce possible environmental problems, and this requires more sodium sulfate. It has also been used to slightly substitute for higher priced zeolites and surfactants when possible because of its lower cost. These factors make the detergent market cyclic and somewhat uncertain, even though throughout the 1990s it has remained as the largest and most dependable portion of the sodium sulfate market. In some formulations burkeite ($2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$) has been suggested in its place to also provide a mild alkali effect.

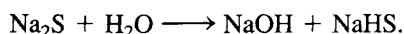
TEXTILE INDUSTRY

Sodium sulfate is used in many applications for the dyeing of textiles. When wool or cotton is dyed with acid colors at temperatures near the boiling point, the dye bath may contain up to 5–10% sodium sulfate (of the weight of the fiber introduced into the bath). More sodium sulfate is used with dark colors than when dyeing lighter

colored fabrics. Certain cationic dye leveling and retarding agents for acrylics and fiber blends may also be utilized with as much as 10% sodium sulfate of the weight of the fiber (Anon., 1981a). The sodium sulfate aids in producing a more “level” color and better distribution of the dye on the fiber (improving the dye’s “standardization”), allowing for a more dilute but equally effective dye strength, and forming a more uniform ionic strength solution. It usually increases the solubility of the dye in the solution, but in the presence of the fabric aids in “salting out” the dye and bonding it to the fiber. It can be blended with concentrated dyes before being added to the vats in order to make them more easily measured, and it precipitates with some organic contaminants. Finally, it is much less corrosive to the dyeing equipment than salt or other solutes that have been used in the past for somewhat the same purposes (Anon., 1998b). Very pure sodium sulfate is preferred for this application so as to not introduce other color agents, or interfere with the dyeing action.

KRAFT (SULFATE OR ALKALINE) PULPING PROCESS

The dominant method of converting wood chips into paper is by the kraft (also called the sulfate or alkaline) process (Kleinert, 1968). The principal chemical raw material used in this process is sodium sulfate, although it becomes converted in the actual pulping solution to primarily sodium hydroxide, sodium sulfide, and sodium carbonate (Table 5.2). The process involves a complex cyclic system (Hornftvedt and Edmark, 1977; Anon., 1970) as shown in Fig. 5.2, where the wood chips are chemically broken down (pulped) in a continuous high-pressure digester at elevated temperatures with “white liquor.” This solution dissolves much of the lignin binder and carbohydrates in the wood, but leaves the cellulose fiber, which is the desired material to form paper. The measure of the effective strength of the white liquor is based upon its content of sodium hydroxide plus half of its sodium sulfide, since the sulfide later becomes hydrolyzed to form more hydroxide:

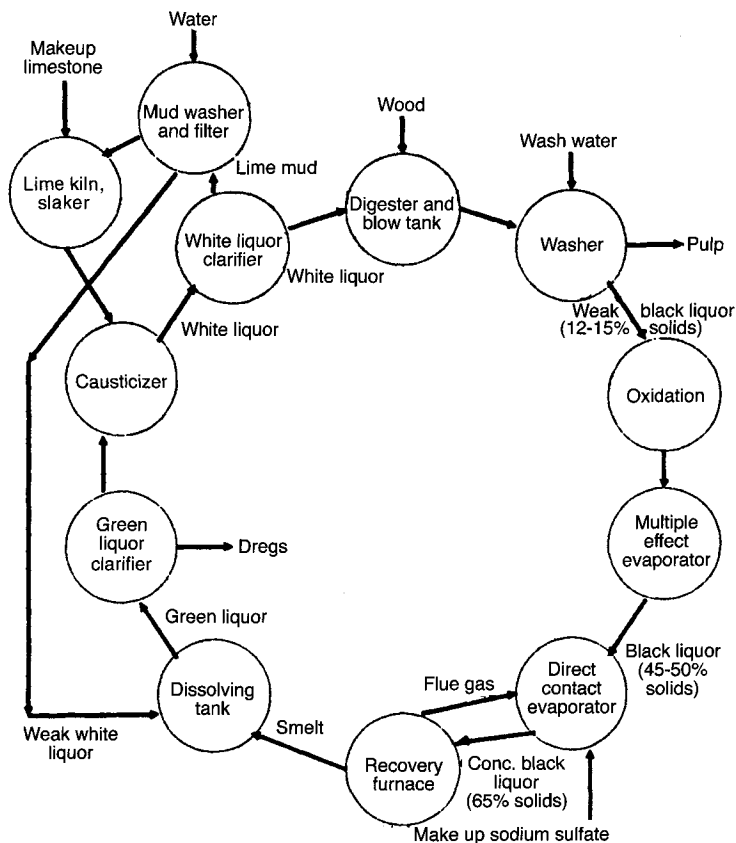


Various other compounds that are present in the white liquor also provide some assistance to the pulping process, but their value is comparatively small. The effectiveness of these chemicals in the digestion liquor and the pulping yield are

Table 5.2
Typical Composition of Kraft Process White Liquor^a

Compound	Na ₂ O content, g/liter	Compound	Na ₂ O content, g/liter
NaOH	73.0	Na ₂ SO ₄	0.6
Na ₂ S	31.4	Na ₂ S ₂ O ₃	0.4
Na ₂ CO ₃	18.2	Na ₂ SO ₃	0.2

^aFrom Garrett, 1992.



measured by the percentage of the fibers that they liberate from the wood, and the fibers' purity and size.

After the wood has been digested, the remaining "weak black liquor" is drained from the pulp, and the pulp is thoroughly washed. The washings are added to the spent digestion liquor, and this solution containing 12–15% solids is first air-blown to partially oxidize some of the compounds that are present, and then evaporated in multiple-effect evaporators to 45–50% solids. At that concentration it is generally considered to be too viscous, have too high a boiling point, and be too near the salts' crystallization point to be further evaporated in forced circulation or "falling film" equipment (Frederick *et al.*, 1980). Consequently it is usually next contacted directly by flue gas in spray evaporators to bring the solids content to 65–70%. Burkeite ($2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$), thenardite (Na_2SO_4), and thermonatrite ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$) scale tends to deposit in the evaporators, so various methods are employed to minimize their formation and adherence to the vessel or tube walls (Branch and Mueller-Steinhagen,

1995; Hedrick and Kent, 1992; Rosier, 1997; Vaistomaa *et al.*, 1996). To make up for chemicals lost in the process, sodium sulfate is next added to the black liquor, and the slurry is sprayed into a special combustion furnace. Here the lignin and other organics in the black liquor burn, producing enough heat to supply the plant's steam, heat, and power needs (and often an excess to be sold). The lower section of the combustion furnace operates under reducing conditions so that the principal constituents of the molten residue ("smelt") are sodium sulfide (Na_2S) and sodium carbonate (Na_2CO_3 ; Mikkonen *et al.*, 1996). The upper section is changed to an oxidizing atmosphere to complete the combustion and convert most of the sulfur-containing gaseous compounds to SO_2 .

As much as 10% of the sodium salts in the liquor volatilizes at the 1250°C temperature of the furnace, so the final section is cooled to condense most of these fumes as a Na_2SO_4 , Na_2CO_3 , and sodium sulfite (Na_2SO_3) dust. This mixture is then blown off and removed from the flue gas, while the sulfur dioxide (SO_2) and other gaseous contaminants are scrubbed by a dilute alkali solution. Both the dust and scrubbing solution are then returned to the black liquor for evaporation and re-reduction to the sulfide and carbonate smelt. Very careful control is required in the furnace to prevent undesired compounds from forming, and also to prevent explosions if some of the black liquor contacts the smelt.

The molten salts are continuously removed from the furnace and sent to a vigorously agitated dissolving tank where they go into solution with wash water from the later-produced muds of the causticizing reaction. The "green liquor" that is produced owes its color to a suspension of insolubles ("dregs") consisting of calcium carbonate and various metal oxides and silicates (Bist *et al.*, 1981). The dregs are settled and removed, and lime is added to the clarified solution to convert most of the sodium carbonate to sodium hydroxide. The calcium carbonate that is also formed is settled, removed, washed, and filtered, and then sent to a kiln to be decomposed back into lime. The clarified "white liquor" is adjusted in strength and returned to the wood chip digester. In this manner most of the feed sodium sulfate is recycled, except for unavoidable losses, including that in a bleed stream to remove various undesired salts such as sodium chloride.

Initially more than 140–180 kg of sodium sulfate were required per ton of pulp produced, but with ever-increasing recycle efficiencies, in 1981 the average U.S. make-up amount was down to 40 kg/t, in 1992 18 kg/t, and it was estimated to possibly reach as low as 5–7 kg/ton (Anon., 1992). Further sodium sulfate reduction has also occurred because other pulping processes have grown in popularity to compete with the kraft process, and when the prices are favorable emulsified sulfur and caustic soda can be used as a sodium sulfate substitute. Also, some by-product sodium sulfate is formed in the (increasingly popular) chlorine dioxide pulp bleaching process, and the residual liquor can be easily added to the pulping liquor. As a secondary factor, up to 50% of all paper is now obtained by recycling, and thus does not require the use of digestion chemicals. Because of these factors, of the original 120–125 kraft mills in the United States using sodium sulfate, only 40 still were doing so in 1992, and 12 in 1994 (Anon., 1994, 1992).

GLASS

A small but fairly steady amount of sodium sulfate has been used in glassmaking for many years, averaging about 1% of the charge for container glass and 0.5% for flat glass (its major use; up to 7% is added in some formulas; McIlveen and Cheek, 1994; Coope and Harben, 1977). It provides a number of benefits; for example, a small amount is helpful in reacting with, and thus limiting the formation of silica scum on the melter surface. A small amount also tends to increase the speed of melting of the original charge, helps reduce the amount of small unmelted solids in the melt (and thus inhibits crystallization), and improves the workability (by reducing the viscosity) of high-silica glass and glass being formed into more complex shapes. These factors aid in the forming process by enhancing the liberation and removal ("fining," or to some extent the solution) of gases that are trapped in the batch or generated during melting. When larger amounts of sodium sulfate are used, carbon is often added with it to aid in producing SO_2 , which helps in the removal of small entrained gas bubbles in the melt. Sodium sulfate in general suppresses the pink color of any selenium impurity that may be present and is a necessary ingredient of some special glasses (i.e., glass for some light bulbs and tumblers: 72.5% SiO_2 , 15.9% Na_2O , 6.5% CaO , 3.0% MgO , 1.3% Al_2O_3 , 0.3% K_2O , and 0.3% SO_2). It is also usually slightly less expensive than soda ash and may be used as a replacement for a small amount of it in the batch.

Cole (1926) also noted a few other advantages to the glass that is produced when sodium sulfate is used. A substantial addition allows higher temperatures to be used in the glassmelting furnace, and thus the amount of silica sand can be increased, which lowers the cost of the glass. When the same furnace conditions are used with and without sodium sulfate, the sodium sulfate glass is harder, has a higher softening point, has greater strength, and is less viscous at 845°C. It has also been found to be a necessary ingredient for glass containing more than 8% lime. Under special conditions bottle and other container glass may use up to 20 kg/mt of glass, whereas window or plate glass may use up to 20–25% of the batch as sodium sulfate, along with an equivalent amount of carbon (coal or coke) as a reductant.

The mechanisms taking place with sodium sulfate in glass furnaces that results in these benefits have been discussed by Rueffel (1970). Sodium sulfate reacts with the silica scum on the vat's surface to form additional sodium silicate glass, along with sulfur trioxide or sulfur dioxide and oxygen, which aid in the mixing process. As the furnace initially heats, at temperatures of about 1040°C the sodium sulfate is molten but the other components are not. It then accumulates on the other solid surfaces to assist in the melting process, thus increasing the rate of melting and the liberation of entrained gas. Above about 1320°C some decomposition of sodium sulfate occurs, and above about 1450°C some vaporization of the sodium sulfate begins, which forms additional gas bubbles that help to homogenize the melt. The sodium sulfate also reduces the viscosity of the melt, which further aids in melting and allowing the gas to escape.

However, on the negative side, the SO_2 or SO_3 that are formed during sodium sulfate's decomposition are corrosive, environmentally regulated gases and must be at least partly removed from the vented flue gas. Also, even if not decomposed, up to 50% of it may be volatilized and must be collected (along with vaporized sodium carbonate) in efficient dust collectors. Finally, sodium sulfate is corrosive to some furnace brick linings, which can result in an iron discoloration to the glass, resulting in further use restrictions (particularly for flint glass). In general a low-iron ($<0.15\% \text{Fe}_2\text{O}_3$) and low-sodium-chloride ($<0.3\% \text{NaCl}$) sodium sulfate is specified when it is to be used in glassmaking (Toon, 1986).

PRODUCTION OF OTHER CHEMICALS

Sodium Sulfide

A number of other chemicals are made from sodium sulfate, such as sodium sulfide (Na_2S). It is produced by the reduction of sodium sulfate with coal, lignite, natural gas, hydrogen, or other reductants in rather simple fusion furnaces at temperatures above 950°C (Cameron and Grace, 1983; Kiyosu, 1980; Nyman and O'Brien, 1947; Puttagunta *et al.*, 1970). Careful control of the reaction conditions is required to produce a fairly pure product and to minimize the amount of unreacted sodium sulfate and the formation of other sulfur and carbonate compounds. The product is drawn off as a melt, solidified, and sold as is, or dissolved and further purified. Its greatest use is in the tanning industry, where great purity is not required, and thus a crude sodium sulfate raw material can be utilized.

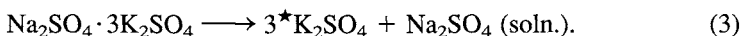
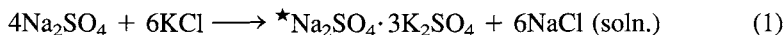
Sodium Carbonate or Bicarbonate

Sodium carbonate or bicarbonate can also be made from sodium sulfate by a modified Solvay process, but is only economically practical when there are protective freight rates, ammonia is relatively inexpensive, and the by-product ammonium sulfate that is formed has a good market. This was done during the early 1990s on a pilot-plant scale by one of the Canadian operators, and may have a limited application in a few other areas. A sodium sulfate brine, or dissolved mirabilite or sodium sulfate, is first purified by adding soda ash to precipitate any calcium and magnesium that may be present. It is then passed through a slightly cooled absorption tower in a countercurrent manner, with ammonia introduced at its base. The resultant ammoniated brine is next passed through parallel groups of well-cooled towers in series, with a counterflow of brine at the top and carbon dioxide from lime kilns, MEA units, etc. (or even flue gas), passing up from the bottom. Sodium bicarbonate precipitates in the final towers, and any ammonia coming off the top is sent to be reabsorbed in the initial, or ammonia tower. The exiting slurry from the bottom of the towers is filtered, and the washed sodium bicarbonate dried and sold as is, or

calcined, rehydrated to the monohydrate, and centrifuged and dried to form dense soda ash. The filtrate is then evaporated to crystallize ammonium sulfate as a valuable coproduct. (The solution could also be reacted with lime to regenerate the ammonia and form calcium sulfate, but under most circumstances this would be very uneconomic). The process is expensive, complex, and most effectively practiced on a large scale to minimize the effects of the high capital and operating costs.

Potassium Sulfate

The production of potassium sulfate has been a commonly considered use for sodium sulfate or various of its double salts. There have been or are plants employing these raw materials at Searles Lake (California) and the Gulf of Kara Bogaz (Turkmenistan). Similar plants have been announced in Canada (50,000 t/yr at Big Quill Lake) and in Turkey (by a joint venture of Alkim and the Dead Sea Works, Israel; 150,000 t/yr of potassium sulfate, 80,000 t/yr of table salt, and 125,000 t/yr of gypsum in a \$40 million [U.S.] plant). The conversion process involves the formation of glaserite ($3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$) as an intermediate salt as shown here in reaction (1), and then either the reaction of glaserite with more potash (2), or simply leaching it (3) to form the desired potassium sulfate:



The reactions proceed rapidly and with reasonable yields, and the end liquor from reactions (2) or (3) is used in reaction (1) to decrease the losses. Even so, the dissolved Na_2SO_4 and KCl in the end liquor of reaction (1) is still appreciable, and the recovery of these salts is almost always required for the process to be economical. This is most simply accomplished by first cooling the brine to crystallize glaserite and glauber salt (to be recycled), evaporating the residual liquor to crystallize salt (to be discarded or sold), and then recycling the end liquor back to the cooling step or to reaction (1). If solar ponds are available, however, by far the least expensive procedure is to send the reaction (1) end liquor to the ponds to be evaporated to dryness, and then separating the deposited (and harvested) salts by flotation to reject (or sell) the sodium chloride. This recycle method will bring some additional insolubles to the process, but insolubles will always be present in any case, since most of the solids entering with the feed materials follow through to the product. The feed material, intermediate, and final products are all solid phases, so only the heaviest insolubles can be settled, or the lightest ones decanted with the end liquor.

Figure 7.12 shows a phase diagram for the process, and Fig. 5.3 is a typical material balance when starting with thenardite (Na_2SO_4) and using solar ponds for

*Less the appreciable K_2SO_4 that dissolves in the solution.

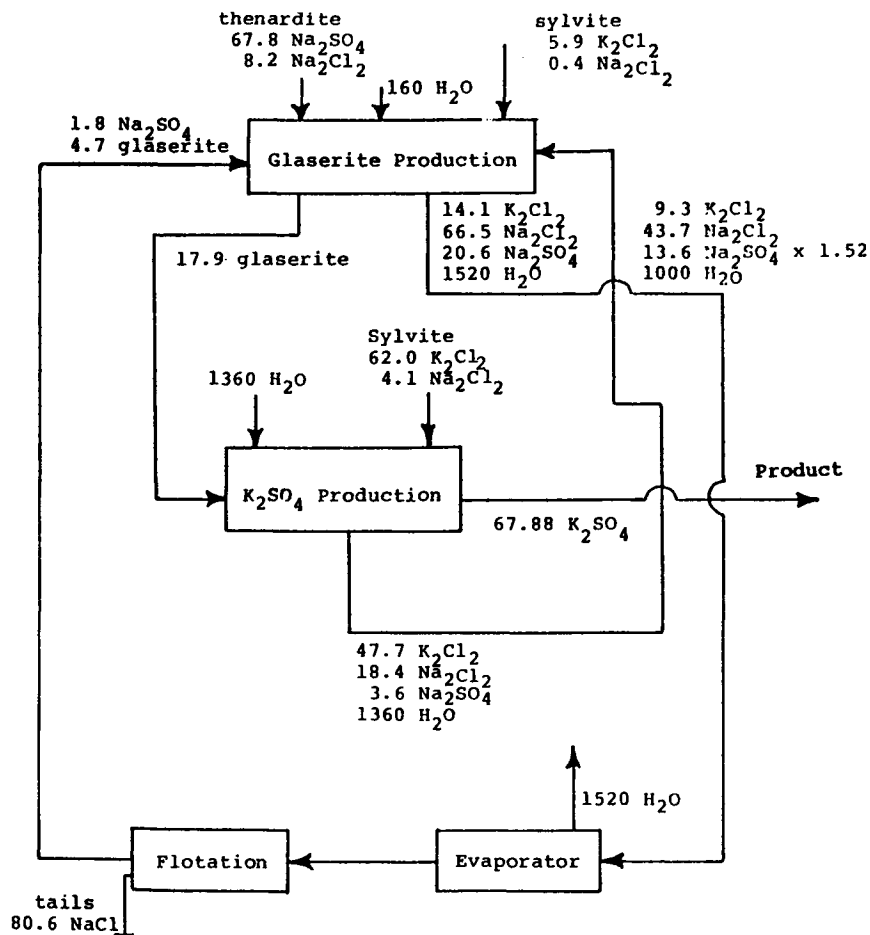


Figure 5.3 Material balance for the glaserite process to make potassium sulfate. (All figures in moles). From Garrett, 1996, courtesy of Kluwer Academic Publishers. See also Chemtob, 1975.

the end liquor. It can be seen that some sodium chloride (or sodium carbonate, if burkeite $[2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3]$ is the feed material) is valuable in improving the yield in the glaserite formation step. However, only a small amount can be tolerated in the conversion of glaserite to potassium sulfate (5% is an absolute maximum, and even 4% requires five times as much KCl as when the NaCl is at 1%). Typical analyses of various liquors in this process when utilizing glauber salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and potash (KCl) as the raw materials, and cooling–evaporation recycle of the end liquor for a 30,000 t/yr Canadian plant (PCS; Storer, 1986), a 60,000 t/yr Kara Bogaz plant (Sokolov *et al.*, 1980), and the Searles Lake plants (Anon., 1955) are shown in Table 5.3. The PCS product had a wide range of crystal

Table 5.3

Process Requirements for the Production of Potassium Sulfate (Garrett, 1996)

A. PCS typical feedstock and product analyses ^b				
Analysis (Wt.%)	Feedstocks		Products	
	Glauber's salt	Muriate of potash	Potassium sulfate	Sodium chloride
Sodium	12.2	1.30	0.58	38.5
Potassium		50.24	43.64	0.9
Calcium	0.1	0.04		
Magnesium	0.1			
Chloride	0.4	47.74	0.27	59.6
Sulfate	25.5	0.08	53.21	0.7
Water	60.1	0.09		
Insolubles	1.6	0.45	1.0	
B. Typical operating requirements for 30,000 tpa plant				
Component	Required for 1 t K ₂ SO ₄			
	Canada ^b		Russia ^a	
Muriate of potash, 60% K ₂ O	0.89 t		0.82 t	
Glauber's salt, 25.5% SO ₄ , 12.4% free water, or Na ₂ SO ₄	2.13 t			
	0.80 t		0.84 t	
Electricity	0.94 GJ		0.24 kw hr	
Natural gas	16.7 m ³		0.01 t oil	
Steam, 930 kPa	2.25 GJ		1.21 g cal	
Process water make-up	None		110 m ³	
Cooling brine, 25°C	39 m ³		None	
By-product salt	0.55 t		0.66 t	
C. Liquor compositions in the Russian glaserite-K ₂ SO ₄ process at 20–25°C (wt. %) ^a				
K ₂ SO ₄ end liquor	Glaserite end liquor			
	As formed	After cooling	After evaporation	
KCl	21	18–20	7–8	15–16
Na ₂ SO ₄	2–3	4–6	1–2	2–4
NaCl	2–5	5–8	19–20	17–18
D. An example of Searles Lake potassium sulfate liquors (when using burkeite feed) (wt. %) ^c				
Refined potash bleed		K ₂ SO ₄ end liquor	Glaserite end liquor	
KCl	26.79	23.43		18.53
NaCl	0.48	2.49		5.28
KBr	0.15	0.16		0.22

(continues)

Table 5.3
(continued)

	Refined potash bleed	K ₂ SO ₄ end liquor	Glaserite end liquor
Na ₂ CO ₃	0.15	0.38	4.27
Na ₂ SO ₄	0.40	1.98	4.24
Na ₂ B ₄ O ₇	0.30	0.30	0.78

^aSokolov *et al.* (1980).

^bAdapted from Storer (1986).

^cFrom Anon. (1955).

sizes, and the Russian product appeared to have small crystals, but with better crystallizer design the Searles Lake product was large and uniform. The residence time for the glaserite formation step in Russia was 50–60 min, although a range of 15–60 min was said to be acceptable. The temperature of both reactions was kept at 20–25°C, with a range of 15–50°C allowable. Their end liquor was cooled to 3 to –8°C to recycle the sulfate compounds and was then evaporated, and after salt (NaCl) removal the residual liquor was returned to the glaserite formation reactor. This gave a high yield for both reactants, but without the cooling–evaporation recycle the yield was only 70%.

At Searles Lake potash was used from 1939 to 1940 with sodium sulfate, from 1940 to 1950 with burkeite, and from then on with any or all of glauher salt (from the winter spraying of lake brine), burkeite, or sodium sulfate, depending upon their availability. All were used as filter cakes (or moist glauher salt), and low-KCl or Na₂SO₄ end liquors from other plants were also employed as raw materials. The glaserite end liquor was returned to the main plant evaporators for recycling. Because of some foaming caused by organics in the lake brine, the potassium sulfate tended to float when settled and thickened prior to being filtered. To solve this problem a novel settler with both a cone bottom and cone top was utilized. When kept full of slurry the K₂SO₄ could settle and be removed at both the top and bottom (Garrett, 1996).

Process descriptions of many other plants or development studies for the production of potassium sulfate from sodium sulfate raw materials with potash can be found in the literature. Most of them are based on the design of adjacent plants, or the raw materials available, as indicated in a few typical articles included in the Processing chapter's reference list.

OTHER USES

There are a very large number of other uses for sodium sulfate, some of which are noted here. Some *carpet cleaning and deodorant* formulations have used up to 85% sodium sulfate, and at times consumed a considerable amount of product (Anon.,

1994). Sodium sulfate is also often used in *cattle feed* mixtures as a source of nutritionally needed sulfur (to aid in the production of proteins, etc.). In larger doses it may also be used by veterinarians as a purgative (laxative) for cattle, horses, and sheep. *Cellulose sponges* have been made in the past by incorporating glauher salt into the viscose cellulose melt. The sponge is slightly heated in a mold to polymerize and solidify the cellulose, and then further heated, washed, and rinsed to melt and remove the sodium sulfate. Some *electroplating* formulas utilize sodium sulfate in the plating baths since it tends to increase the conductivity of the solution, and thus reduce the voltage requirement. Sodium sulfate can be added to low-sulfur coal to improve the efficiency of high-temperature *electrostatic precipitators* (Anon., 1980). *Energy storage* using the phase change of glauher salt to its solution has been extensively studied and, if the settling problem can be overcome holds considerable promise for refrigerators and other cooling systems (Goldstick, 1979; Anon., 1984a). In *nickel refining* the Oxford process employed sodium sulfate with coal (to form sodium sulfide) to melt with the sulfide ore "matte." Most of the nickel sulfide selectively sank to the bottom of the cupola furnace and could be drawn off with only a modest iron and copper content. The *pigments* ultramarine and Prussian Blue use sodium sulfate in their manufacture, as do certain *inks* (Cole, 1926). It is also used in the spinning bath in the manufacture of *viscose rayon*, in *phosphoric acid purification* (Anon., 1984b) and as a *concrete additive* (Pashchenko *et al.*, 1985).

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Estimates of the natural sodium sulfate production rates for various countries, as made by the U.S. Geological Survey (Kostic, 1999–1979) are listed in Table 6.1, and the world total is plotted in Fig. 6.1. Unfortunately, the numbers have a very mixed degree of accuracy, since some are the result of careful surveys or company reports, and others are only educated guesses based on limited published information. When the reported numbers change rapidly, such as 1991–1992 for China and Chile, the change is often based upon new information for the estimate, and not necessarily a change in production. In a similar manner, round numbers or steady values are often indicative of somewhat uncertain guesses. However, if it is assumed that the values for the total natural sodium sulfate production (the sum for all of the countries) are roughly correct, then there has been a fairly steady growth in production from 1974 through 1996 of 1.8% per year.

Data on the total, worldwide production of all sources of sodium sulfate (natural, synthetic, and by-product) are shown in Table 6.2 and Fig. 6.2. It is seen that there has been a fairly steady increase in the world's total production rate, averaging 1.2%/yr from 1973 to 1996. At the same time, the production of synthetic and by-product sodium sulfate (Table 6.2, Fig. 6.2) has remained nearly constant (or perhaps a 0.56%/yr growth rate over this period), allowing the increase in the world's total sodium sulfate market to have been primarily with the natural product.

Since the 1970s there has been a significant shift in the production pattern for natural sodium sulfate among the different countries. The previous major producers, the United States, Canada, and the former Soviet Union (particularly Turkmenistan) have now considerably reduced their output, while Spain, Mexico, and China have greatly expanded their production. The declines in the U.S. and Canadian production (both at $-2.7\%/yr$ from 1971 to 1996 or 1974 to 1997; Figs. 6.2 and 6.4, respectively) have been caused by a major reduction in the U.S. and Canadian sodium sulfate consumption (for the United States, $-3.3\%/yr$ from 1968 to 1998; Table 6.3 and Fig. 6.3), while the decline in Turkmenistan resulted from damage to the Gulf of Kara Bogaz deposit. The increased production in Spain and Mexico

Table 6.1

World Production of Natural Sodium Sulfate (1000 mt) (Kostic 1999–1979; others)

	1999 ^a	1997	1996	1995	1994	1993	1992	1991	1990	1989
United States	320	318	306	327	298	327	337	354	349	340
Argentina	15	15	22	11	8	7	25	16	11	10
Canada	350	305	323	311	317	320	282	332	345	323
Chile ^b	150	60	60	60	60	60	60	13	14	10
China ^b	300	300	250	200	200	200	150	28	27	27
Egypt	25	25	25	25	25	26	41	41	41	46
Iran	180	280	280	280	280	280	237	144	177	185
Mexico	600	525	525	500	527	500	534	518	545	478
South Africa	35	55	47	44	45	36	37	30	20	15
Spain	900	700	630	638	600	650	675	700	716	539
Turkey	182	200 ^b	200	214	207	123	75	115	110	68
Russia ^b	40	100	100	100	100	100	100	320	340	365
Others	20	20	20	20	20	20	22	10	10	10
Total	3117	2903	2788	2730	2687	2649	2575	2621	2709	2416
	1988	1987	1986	1985	1984	1983	1982	1981	1980	1979
United States	361	347	360	353	395	384	463 ^a	541	530	485
Argentina	15	27	32	40	45	45	43	41	38	44
Canada	331	342	371	375	387	454	547	455	500	377
Chile	16	12	5	64	64	64	1	5	5	22
China	27	18	14	30	30	30	30	30	30	30
Egypt	42	42	19	5	5	5	3	4	4	4
Iran	214	264	123	18	18	18	10	14	9	23
Mexico	422	486	457	420	414	396	426	409	400	331
Spain	450	475	451	330	367	313	211	182	221	270
Turkey	79	83	59	85	83	62	65	55	48	53
Russia	375	365	345	370	360	360	361	355	350	341
Others	10	10	20	15	16	14	5	10	10	10
Total	2342	2450	2255	2105	2184	2145	2220	2101	2145	1990
	1978	1977	1976	1975	1974	1973	1972	1971	1970	1969
United States	550	578	603	606	620	610	636	624	542	566
Argentina	43	36	35							
Canada	415	395	461			700?				
Chile	20	14	15							
China	30 ^a	30 ^a	30 ^a							
Egypt	3	6	4							
Iran	39	40	25							
Mexico	298	261	251	246		161	136	124	128	108
Spain	208	182	165				73			
Turkey	71	73	88							
Russia	365	318	309							
Others	10 ^a	10 ^a	10 ^a							
Total	2052	1943	1996	1971	1944	1770	1649	1391		

^aValues estimated by the author.^bThe period 1999 through 1992 consists of estimates by the author, including Kara Bogaz, Turkmenistan.

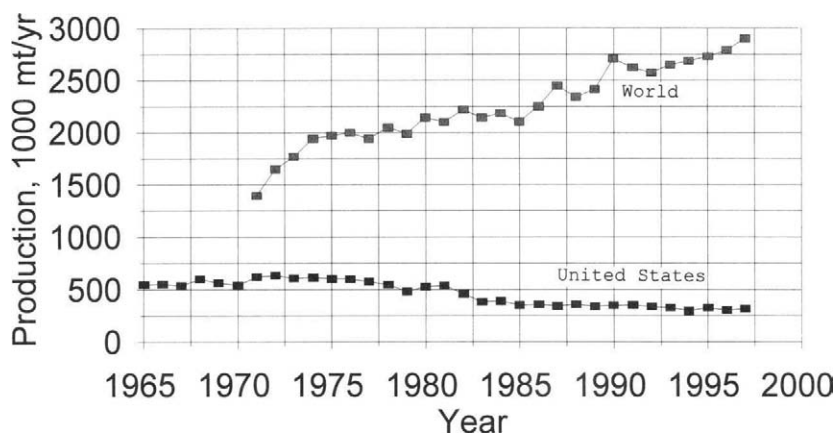


Figure 6.1 Estimated United States and world natural sodium sulfate production. (From Kostic, 1999–1979, others.)

has resulted from the aggressive exploitation of very large deposits and the just-noted general expansion of the world's economy and sodium sulfate consumption. The expansion of the natural sodium sulfate plants was also based on their producing a very high-quality product, which has put pressure on the production of synthetic sodium sulfate (made for its value alone, such as from Mannheim furnaces converting salt and sulfuric acid to Na_2SO_4 and HCl). In a similar manner the very large amount of by-product sodium sulfate (such as from rayon or chrome chemical

Table 6.2
Estimated Total U.S. and World Sodium Sulfate Production (1000 mt/yr)
(Natural, By-Product and Synthetic; Kostic, 1999–1979)

	1997	1996	1995	1994	1993	1992	1991	1990	1989
United States	580	602	645	591	537	553	720	713	685
World Synth., Byprd.	2617	2582	2580	2493	2331	2055	2049	2348	2452
World Production	5520	5370	5310	5180	4980	4630	4720	5057	4868
	1988	1987	1986	1985	1984	1983	1982	1981	1980
United States	743	725	763	736	791	776	784	1008	1003
World Synth., Byprd.	2520	2455	2354	2404	2218	1937	1901	2600	2386
World Production	4862	4895	4609	4509	4402	4082	4121	4701	4531
	1979	1978	1977	1976	1975	1974	1973	1972	1971
United States	1017	1060	1088	1113	1223	1305	1204	1231	1246
World Synth., Byprd.	2540	2274	2236	2466	2472	2188	2270	2119	
World Production	4530	4326	4179	4462	4443	4132	4040	3768	

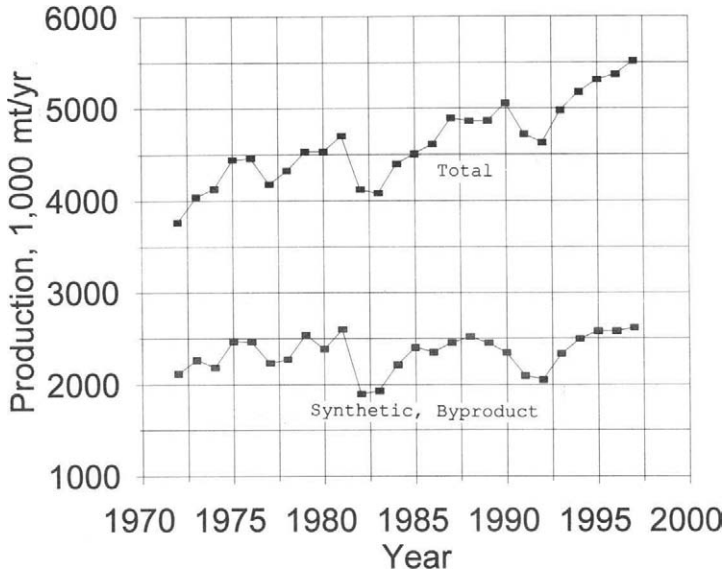


Figure 6.2 Total sodium sulfate, and synthetic plus by-product production. (From Kostic, 1999–1979; others.)

plants) suffers from the swings in the demand for their primary products, and their sodium sulfate has had to be upgraded or be sold at a lower price.

The United States' production of natural sodium sulfate (Tables 6.1 to 6.3; Figs. 6.1 and 6.3), as previously noted, has decreased by 2.7%/yr from 1971 to 1996, but held fairly steady since about 1985 (perhaps $-0.87\%/yr$). The yearly U.S. production of both natural and other sodium sulfate, and the country's consumption, exports, and imports, are listed in Table 6.3. In the early days of the U.S. industry the production of natural sodium sulfate rose steadily to its maximum of 636,000 mt in 1972 at an average growth rate of 4.5%/yr from 1942 to 1972, and since then has steadily declined. Synthetic and by-product sodium sulfate production steadily rose to its maximum of 772,000 mt in 1969, and then has also declined at an even faster rate ($-3.9\%/yr$ from 1969 to 1997). Imports steadily rose until they reached a maximum of 329,000 mt in 1974 (perhaps exceeded in 1982 with 358,000 mt), and then again steadily declined. Exports have been much more erratic, but rose to the +100,000 mt/yr level in the 1980s, had one spurt to 155,000 mt in 1992, but have been generally holding steady or slightly declining in the 1990s. The total U.S. consumption of sodium sulfate reached a peak of 1,554,000 mt in 1973 and has rapidly declined to about one-third that value since then ($-3.3\%/yr$ from 1968 to 1998). The detergent market for many years has been the largest U.S. consumer of sodium sulfate, but it is subject to variability and reduction because of inroads of liquid and other detergents that use little or no sodium sulfate. This makes the projected 2%/yr

Table 6.3

U.S. Production, Consumption, Exports, and Imports of Sodium Sulfate (1000 mt/yr, or st^a; Kostic, 1999–1979; others)

Production	1998	1997	1996	1995	1994	1993	1992	1991	1990	1989
Natural		318	306	327	298	327	337	354	349	340
Synthetic		262	296	318	293	210	216	366	364	245
Imports		150	177	206	190	163	158	157	162	173
Exports		86	86	66	65	89	155	103	62	62
Consumption	586	644	693	785	716	611	556	774	813	796
Production	1988	1987	1986	1985	1984	1983	1982	1981	1980	1979
Natural	361	346	359	353	395	384		552	529	484
Synthetic	382	379	404	383	396	392		456	504	533
Imports	136	125	171	176	164	312	358	250	209	171
Exports	77	111	100	108	109	83	101	113	117	93
Consumption	802	739	834	804	846	1005	1073	1145	1125	1095
Production	1978	1977	1976	1975	1974	1973	1972	1971	1970	1969
Natural	549	577	601	605	621	610	636	624	543	566
Synthetic	511	511	516	508	602	695	568	607	703	772
Imports	124	202	287	258	329	290	271	244	244	259
Exports	76	39	52	70	46	41	26	60	50	82
Consumption	1108	1251	1352	1321	1506	1554	1449	1415	1440	1515
Production	1968	1967	1966	1965	1964	1963	1962	1961	1960	1959
Natural	599	539	556	551	493	395	416	424	409	366
Synthetic	746	698	755	722	701	725	693	608	590	621
Imports	277	263	216	248	262	146	170	178	151	111
Exports	51	25	26	12	40	41	46	29	28	20
Consumption	1571	1475	1501	1509	1416	1225	1233	1181	1122	1078
Production	1958	1957	1956	1955	1954	1953	1952	1951	1950	1949
Natural	315	301	303	299	227	225	213	240	170	169
Synthetic	546	650	680	705	616	722	645	705	582	320
Imports	88	67	116	113	108	55	51	74	61	19
Exports	18	22	27	23	23	25	25	24	15	4
Consumption	931	996	1072	1094	928	977	884	995	798	504
Production	1948	1947	1946	1945	1944	1943	1942	1941	1940	1939
Natural ^a	266	257	199	178	169	161	170	154	187	137
Synthetic ^a	401	437	329	366		403		377		
Imports ^a	29.6	49.2	22.4	20.3	31.3	32.8	93.7	75.6	73.1	155
Exports ^a	12.4	7.6	8.7	5.6		7.1		0.9		
Consumption ^a	685	735	541	558		590		606		

(continues)

Table 6.3
(continued)

Production	1938	1937	1936	1935	1934	1933	1932	1931	1930	1929
Natural ^a	80.2	80.1	51.6	38.7	16.7	46.5	32.2	32.5	32.6	7.5
Synthetic ^a			184			132				200
Imports ^a	150	237	164	117	98.6	110	70.3	84.0	81.4	98.3
Exports ^a			4.6			0.8				21.3
Consumption ^a			395			288		245		284
Production	1928	1927	1926	1925	1924	1923	1922	1921	1920	1919
Natural ^a	6.6	23.1	19.6	9.9	16.2	10.1	5.0	4.9	14.9	
Imports ^a	33.4	17.2	11.2	8.7	10.0	14.4	7.5	3.2	0.1	
Consumption ^a		335		276		295		170	201	150
	1918	1917	1914	1909						
Imports ^a			0.2							
Consumption ^a	163	205	111	15						

^aValues listed as 1000 short tons for 1948 and earlier.

growth rate (Anon., 1999) for natural sodium sulfate during the early 2000s very uncertain.

The production of sodium sulfate in Canada (Table 6.4 and Fig. 6.4) has somewhat followed the pattern of the United States. It reached a maximum of 565 mt/yr in 1974 (perhaps 700,000 mt/yr in 1973; averaging a growth rate of 5.5%/yr from 1943 to 1974) and another submaximum of 547,000 mt in 1982, and then has experienced a rapid decline (−2.7%/yr from 1974 to 1997) to the low 300,000 mt/yr

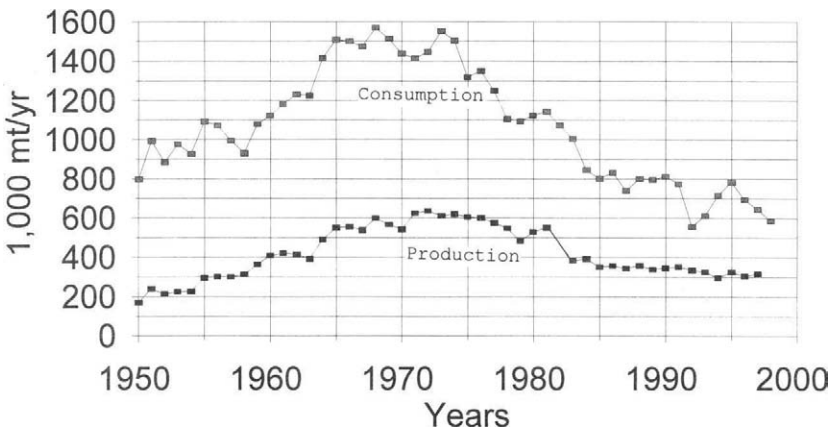


Figure 6.3 United States natural sodium sulfate production, and total sodium sulfate consumption. (From Kostic, 1999–1979; others.)

Table 6.4

Canadian Natural Sodium Sulfate Production (1000 mt/yr, or st^a; Kostic, 1999–1979; others)

1999 ^b	1997	1996	1995	1994	1993	1992	1991	1990	1989	1988	1987	1986
350	305	323	311	317	320	282	332	345	323	331	342	371
1985	1984	1983	1982	1981	1980	1979	1978	1977	1976	1975	1974	1973
375	387	454	547	455	500	377	415	395	461	423	565	700?
1968	1958	1957	1956	1955	1954	1953	1952	1951	1950	1949	1948	1947
425	173 ^a	158	181	179	158	116	123	192	131	120	154	163
1946	1945	1944	1943	1942	1941	1940	1939	1938	1937	1936	1935	1934
106	93	102	107	131	116	94	71	63	80	76	45	67
1933	1932	1931	1930	1929	1928	1927	1926	1925	1924	1923	1922	1921
50	22.5	45.0	31.6	5.0	6.0	5.7	6.8	3.9	1.08	0.73	0.50	0.62
1920												
0.81												

^aFrom 1958 and earlier, the values are in short tons.^bAuthor's estimate.

level in the mid-1990s. However, it has also held fairly steady since about 1988. As with some other countries, a higher percentage of their product is still sold to the local kraft paper mills that do not have quite as much recycling, chlorine dioxide bleaching, etc., as the U.S. mills. The average price of sodium sulfate sold in Canada is also shown in Fig. 6.4, indicating the rapid price increases in the 1970s as the product quality increased and the volume decreased.

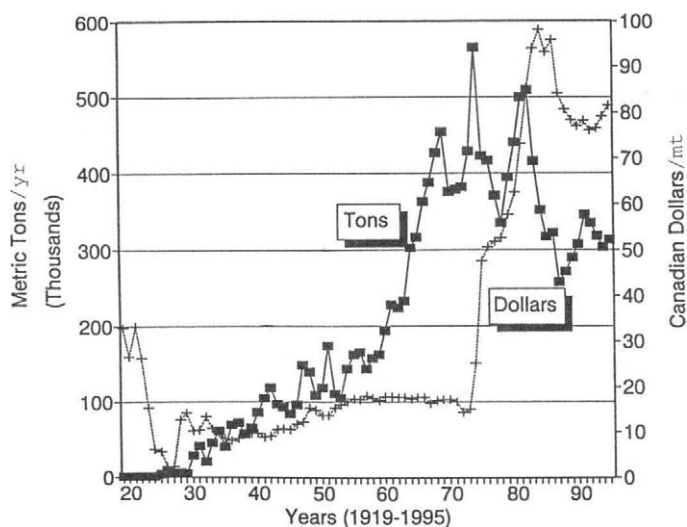


Figure 6.4 Saskatchewan Canada's natural sodium sulfate production and average price. (From Murphy, 1996, with permission of the North Dakota Geological Survey.)

Table 6.5
Yearly Average Price of U.S. Sodium Sulfate (\$/mt) (or st^a; Kostic, 1999–1979, others)

		1997	1996	1995	1994	1993	1992	1991	1990
		109.13	88.90	84.55	81.25	76.53	91.79	87.34	96.63
1989	1988	1987	1986	1985	1984	1983	1982	1981	1980
91.55	86.87	95.69	94.92	101.62	101.59	101.85	91.49	78.30	68.81
1979	1978	1977	1976	1975	1974	1973	1972	1971	1970
61.39	50.77	50.81	54.29	45.72	26.44	19.03	17.92	17.64	20.15
1969 ^{a,b}	1968	1967	1966	1965	1964	1963	1962	1961	1960
18	18	17	17.5	18	18.5	19	20	20	19
1959	1958	1957	1956	1955	1954	1953	1952	1951	1950
19	19.35	19.76	19.36	18.91	15.58	13.46	13.58	8.81	11.79
1949	1948	1947	1946	1945	1944	1943	1942	1941	1940
14.68	15.98	12.94	8.53	8.56	9.34	9.67	9.83	9.35	8.16
1939	1938	1937	1936	1935	1934	1933	1932	1931	1930
7.48	7.44	7.49	6.52	7.13	8.90	5.27	6.53	6.09	6.32
1929	1928	1927	1926	1925	1924	1923	1922	1921	1920
5.46	6.46	7.32	8.50	8.49	10.78	9.92	7.21	17.35	14.89

^aFrom 1969 and earlier the values are in \$/short ton.
^bThe 1959–1969 values are only accurate to two figures.

The average price of sodium sulfate realized by the producers in the United States is listed in Table 6.5 and shown in Fig. 6.5. After a very long period of being a low-priced, crude, large-tonnage commodity, in the mid-1970s the price began to significantly rise, as in Canada and elsewhere. The consumption had started to

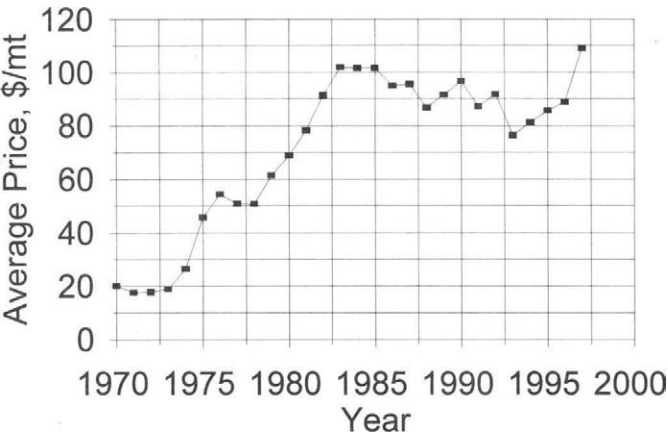


Figure 6.5 Average U.S. sodium sulfate price, as realized by the producer. (From Kostic, 1999–1979; others.)

Table 6.6
Production Capacity of Various Natural Sodium Sulfate Producers
(1000 mt) (Anon., 1999–1991; others)^a

	1999 ¹	1995	1986	1977
<i>Canada</i>				
Saskatchewan Minerals, Chaplin Lake, Sask.	150	140	136	136
Ingebright Lake, Sask.	200	170	136	136
Frederick Lake ² , Bishopric, Sask.	0	—	45	64
Millar Western ³ , Whiteshore Lake, Sask.	80	70	—	90
Francana Minerals, Snakehole Lake ⁴ , Sask.	0	36	90	90
Alsask Lake ⁵ , Sask.	0	0	45	45
Ormiston Mining ⁶ , Horseshoe Lake, Sask.	0	10	70	90
Sotec Products ⁷ , Metiskow Lake, Alberta	0	40	—	90
Sybouts Sodium Sulfate, Sybouts Lake, Sask.	0	—	—	45
<i>Chile</i>				
Sociedad Quimica y Minera de Chile	160	60	60	50
<i>China</i>				
YiKeZhao Chemical Industry	200	200	—	—
Yuncheng Lake, Shanxi	16	16	16	16
<i>Mexico</i>				
Quimica del Rey (Penoles), Coahuillo	620	500	—	—
Sulfato de Viesca	0	22	—	—
<i>Spain</i>				
Minera de Santa Marta, Belorado, Burgos	200	100	0	0
Sulquisa, Villaconejos, Madrid	200	116	90	—
Crimidesa, Rio Tiron, Burgos	500	350	—	—
FMC Foret, Villarrubia de Santiago, Toledo ⁸	200	150	150	73
<i>Turkey</i>				
Alkim: Acigol Lake	163	110 ⁹	90 ⁹	80 ⁹
Konya Lakes, Bolluk Plant (incl. Cayirhan mine)	72	50 ⁹	20 ⁹	18 ⁹
Others: Acigol Lake ⁹	20	20	20	20
<i>United States</i>				
IMC Global ¹⁰ , West End plant, Searles Lake	200	205	214 ¹¹	207
(Kerr-McGee Chemical), Trona plant	0	230	230	230
Cooper Resources ¹² , Seagraves, Texas	140	136	136	95
(Ozark Mahoning), Brownfield, Texas	0	0	64	64
Great Salt Lake Minerals ¹³ , Utah	0	0	36	32

^aKey to footnotes: 1, Anon. (1999), (1998a); also company reports. 2, Frederick Lake closed in 1983, had been Natural Sodium Products. 3, Operation near Palo, had been Midwest Chemicals. 4, Snakehole Lake (Cabri) closed in 1991, had been Midwest Chem. 5, Alsask Lake closed in 1991, had been Sodium Sulfate Co. 6, Closed in 1998, since 1993 there was some pilot plant production of sodium bicarbonate, had been Midwest Chem. 7, Closed in 1997, had been Alberta Sulfate Ltd. and then Francana (owned by Agassiz Resources). 8, Had been Sociedad Union Salmera de Espana until 1986. 9, Author's estimate. 10, Had been American Potash & Chemical Corp., then Kerr McGee Chemicals to 1990, then North American Chemical Co. to 1998. 11, Also quoted as 218 in 1986 and 1994, 227 in 1990, and 204 in 1996. 12, Had been Ozark-Mahoning and then Elf Atochem. Also quoted as 150 in 1999, 141 in 1996 and 1994, and 136 in 1986. 13, Closed a 45,000 mt/yr plant in 1993.

Table 6.7
 Estimated Reserves of Various Sodium Sulfate Deposits
 (Literature or Published Values; 1,000,000 mt Na₂SO₄)

Ancient, buried deposits

Argentina

Cerro Blanco: 1.2 (thenardite)

Canada

New Brunswick: 25 (glauberite)

Chile

Nitrate deposits: 1,200 total in caliche; including
 Soquimich: 100 (?; thenardite, astrakanite)

China

Many deposits: 1–200 (?; glauberite, thenardite, astrakanite)

Mexico

Bacadehuachi: 100 (thenardite)

Former Soviet Union

Kichik-Kul (Aral, Central Asia): 15 (glauberite)

Tien Shan: 4000 (?; glauberite, thenardite, astrakanite)

Many other deposits: 1–100 (?; glauberite, thenardite, astrakanite)

Spain

Madrid, Ebro and Calatayud Basins: 2,500 total; 272 economic (thenardite and glauberite);
 including FMC Foret: 200 total; 50 economic (thenardite), MSM (Minera de Santa Marta):
 225 total 57 economic (glauberite), Sulquisa: 78 economic (glauberite)

Turkey

Cayirhan: 65 (thenardite, glauberite)

United States

Bertram (Salton Sea): 2 (thenardite, astrakanite)

Stewart (Hoover Dam): >2–4 (glauberite)

Verde Valley: 100 (thenardite)

Comparatively recent playas or brine deposits

Antarctica: Yearly deposition; ~4/yr (mirabilite)

Hobbs Glacier: 4 (mirabilite)

Argentina

Colorada Grande: 59 (mirabilite, brine [NaCl byproduct])

Puna Region: 5(?); Santa Cruz Province: 1.2 (mirabilite)

Botswana

Sua Pan: 110 (brine)

Canada: 80 total; 30(?) economic

Alsask: 2.6; Aroma: 1.1; Ceylon: 1.0; Frederick: 2.4; Horseshoe: 3.7; Ingebright 9.0;

Little Manitou: 1.2; Metiskow: 2.3; Muskiki: 3.0¹; Snakehole: 1.7; Sybouts: 3.3;

Verlo East: 1.1; Vincent: 2.0; Whiteshore: 6.5 Lakes (mirabilite)

(continues)

Table 6.7
(continued)

Big Quill: 7.0; Chaplin: 3.0; Dead Moose: 1.6; Freefright: 1.3 Lakes (brine)
Many others (~70): 0.1–1 (mirabilite, brine)
China
Chaganor: 4.5 (brine processed; burkeite deposit)
Pengshan: 4.7 (brine)
Many others: 0.1–100 (mirabilite, brine)

Comparatively recent playas or brine deposits

Egypt
Beida Lake (Wadi Natrun): 1.1 (thenardite)
Lake Qarun: 4 (brine)
India
Didwana: 1.8 (thenardite)
Sambhar Lake: 22 (brine [potential NaCl byproduct])
Tsokar Lake: 1.1 (mirabilite)
Iran
Hoz-I-Soltan: 10(?) (mirabilite, brine)
Mexico
Laguna del Rey: 350 (brine processed; glauberite, astrakanite deposit)
Namibia
Otjiwalunda Playa: 80 (thenardite, burkeite)
Peru
Laguna Salinas: 3 (mirabilite)
Former Soviet Union
Aral Sea: 200, adjacent lakes: 4; Azhbulat Lake: 40; Kachuk Lake: 540;
many others: 1–10 (mirabilite)
Kara Bogaz: 2,000; 10 under production (brine processed; glauberite, astrakanite deposit)
Maloe Yarvoe Lake: 4; many others: 1–10 (mirabilite, brine)
Turkey
Acigol Lake: 12.5 (82 possible); Tersakan Lake: 10 (brine)
United States
California:
Searles Lake: 434 (brine processed); Owens Lake:
9.9 (thenardite, burkeite, brine deposits)
Soda Lake: 1.5; Wabuska: >1 (mirabilite, thenardite)
Dale Lake: 11 (thenardite, brine)
Nevada: Rhodes Marsh: >3 (mirabilite, thenardite)
North Dakota: Total: 19; Grenora Lakes: 6.9; Miller Lake: 5.7 (mirabilite)
Texas: Cedar Lake (Seagraves): 7; Soda Lake (Monahans; now depleted): 2; several others:
1–10 (brine processed; brine deposit, some mirabilite)
Utah: Great Salt Lake: 408 (mirabilite, brine)
Wyoming: Downey Lakes 2; several others; 0.1–2 (mirabilite)

Table 6.8
Typical 1999 Sodium Sulfate Product Specifications

Chemical analysis, wt. %									
	MSM ¹		CNR ²	Sask. Miner. ³		Penoles ⁴			
	Typ. ⁵	Limit		Typical					
				Limit	Ing. ⁶	Chaplin	Limit		
Na ₂ SO ₄	99.7 ⁷	99.5 ⁸	99.5 ⁸	99.6	99.4	98.5 ⁸			
NaCl	0.10	0.30 ⁹	0.20 ⁹	0.12	0.15	0.50 ⁹			
Ca	0.01	0.03 ⁹	—	0.01	0.02	—			
Mg	0.01	0.03 ⁹	0.02 ⁹	0.04	0.05	0.16 ⁹			
Insol. ¹⁰	0.005	0.01 ⁹	0.05 ⁹	0.01	0.01	0.10 ⁹			
Moisture	0.02	0.05 ⁹	0.02 ⁹	0.02	0.02	0.10 ⁹			
Fe, ppm	2 ¹¹	5 ^{9,11}	3 ⁹	6	3	35 ⁹			
Metals ¹²	<1	1 ⁹	—	< 0.5 ¹³	< .2 ¹⁴	—			
Color	5 ¹⁵	—	White	90.8 ¹⁶	92.0 ¹⁶	White			
pH, 1% sol.	7	6.5–7.5	7–7+	7.9 ¹⁷	8.5 ¹⁸	—			
Bulk dens. ¹⁹	1.4	1.3–1.5	1.4–1.55	1.3 ²⁰	1.35	1.4g/cc			
Melt.pt.	—	—	888°C	882	882	880–888°C			
Other	—	—	—	NaHCO ₃ : 0.06	0.09	—			
				Na ₂ CO ₃ :	0.06	—			
Screen analysis, wt. %									
Minera de Santa Marta (MSM) ²¹					Sask. Miner.				
Micron	Screen	Std.	Crs.II	Crs.I	Screen	CNR	Ing.	Chap.	Penoles
+1000	+16	—	0	0	+20	0	0.2	0.1	
+500	+32	—	15 ⁸	30 ⁸					
+315	+46	25 ⁹	—	—	+40	1.7	3.1	1.3	5 ²²
315–250	46–60	5 ⁸	—	—					
+250	+60	—	70 ⁸	70 ⁸	+60	23.6	16.6	7.1	
250–125	60–115	35 ⁸	—	—	+80	47.4			
125–100	115–150	5 ⁸	—	—	+100	61.6	46.2	42.1	70
< 100	<150	35 ⁹	5 ⁹	5 ⁹	+140	75.8			
Mean,	micron	210	400	500	+200	89.4	80.9	88.4	
		±50	±50	±50					

^aKey to footnotes: 1, MSM = Minera de Santa Marta. 2, CNR = Cooper Natural Resources. 3, Saskatchewan Minerals. 4, Industrias Penoles. 5, Typ. = typical analysis; Limit = maximum or minimum value. 6, Ing. = Ingebrigt plant. 7, 99.7% for Standard; 99.8% for Coarse, 8, Minimum. 9, Maximum. 10, Water insolubles, except acid insoluble for MSM. 11, For Std.; Crs.: typ.1, limit 2. 12, ppm content of Al, Cd, Co, Cr, Cu, Mn, Ni, Pb, Ti, V. Zn. 13, ppm; Sask.M. also As, B, Hg, K, Sb, Se, Te; K = 120. 14, ppm; K = 161, Al 2.6, B 2.3, 15. 5% Solution; Hazen test. 16, Reflectance; angle of repose = 32°C. 17, 5% solution pH = 8.8; 10% 9.2. 18, 5% solution pH = 9.7; 10% 10.1, 19, Bulk density, g/cc; MSM values for Na-N; GI typ.1.6, limit 1.5–1.7; GII typ.1.5, limit 1.4–1.6. 20, 1.46 tapped. 21, Std. = Standard Na-N; Crs.I = Coarse Na-I; Crs.II = Coarse Na-II. 22, 35 mesh.

dramatically decrease, much more high-purity detergent grade material was being sold, and the quality for most of the other uses was also increased to meet the customer demand and severe competition. This caused prices to rapidly rise, reaching a value of \$102/mt (yearly average price in the U.S.) in 1983, and then fluctuating from \$80 to \$110/mt in the 1980s and 1990s.

The production capacity of some of the world's natural sodium sulfate producers has been estimated in Table 6.6. It is seen that over the period listed several of the companies have steadily increased their capacity, others have held their capacity fairly steady, and some have closed their operations. In general those plants that have expanded produce a high-quality product and have favorable export markets, very large deposits (or ones that are relatively inexpensive to operate), and aggressive managements. In most cases they will probably continue to expand to fill the growing needs, while others will fall to the steadily increasing competition.

The reserves of various of the world's actual and potential sodium sulfate deposits are listed in Table 6.7. Again there is a wide variation in the accuracy of the estimates and in their potential for commercial recovery, with some of the reserve estimates being quite precise, and others very uncertain. The list only includes those deposits where there has been an estimate given in the literature, or there is enough information on the deposit for the author to make an estimate. A very large number of important deposits have not been included in the list because of lack of data. Even so, it can be seen that there are many potentially commercial sodium sulfate deposits in the world. Their recovery in the future will depend primarily on their economic potential based upon size, the ease and cost of processing (including the grade, purity, and mining cost of the ore), the availability and cost of shipping to both domestic and foreign markets, and other cost factors such as by-products, shared marketing costs, and consideration of the operating companies' experience with this type of product.

Typical 1999 sodium sulfate product specifications are shown in Table 6.8 for several producers. Each of these companies make a very pure white product, with little dust and a fairly narrow particle size range.

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PHASE DATA

A very large amount of phase data exists for the aqueous solutions of sodium sulfate, both alone and in combination with other salts. However, since most of this data is not important in the processing of natural sodium sulfate ores, this presentation will be limited to the phase data involved with the most common sodium sulfate minerals: mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), thenardite (Na_2SO_4), glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$), astrakanite ($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$), and burkeite ($2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$), as well as the production of potassium sulfate from sodium sulfate. The units used for all of the simple phase data measurements will be weight percent of the anhydrous salt in a saturated solution of water, whereas the more complex reciprocal salt pair data will sometimes use the units of grams of salt per 100 grams of water, or moles of salt per 1000 moles of water. These latter units simplify the construction of the commonly employed four-sided Janecke phase diagrams.

Table 7.1 and Fig. 7.1 present smoothed phase data for the solubility of pure sodium sulfate in water. Many researchers have published data on this system, and at the lower temperatures there is fairly good agreement on the numbers for at least two-figure accuracy (and often to the first decimal place). Much of this slightly variable data has been plotted together, and the smoothed, most consistent numbers taken from the graph to be listed in Table 7.1 and replotted in Fig. 7.1. The transition temperature of the decahydrate changing to anhydrous sodium sulfate occurs at 32.38°C and 33.20% Na_2SO_4 , numbers that appear to be generally accepted. For the data above about 150°C there is much more variation among the investigators, but they all follow the same general pattern (and there is closer agreement among the two most recent sources), but the exact transition temperature (and Na_2SO_4 concentration) from ortho to mono sodium sulfate is still somewhat uncertain. In a similar manner there is less data on the metastable sodium sulfate heptahydrate solubility, again reducing its accuracy. All of the data has

Table 7.1
Solubility and Density of Sodium Sulfate in Water (wt%) (Seidell, 1965)^a

Temp. (°C)	Na ₂ SO ₄	Density	Temp. (°C)	Na ₂ SO ₄
-1.25 ¹	4.15	—	110	29.58
0 ²	4.31	1.041	120	29.48
5 ²	5.84	1.0575	130	29.53
10 ²	8.26	1.0795	140	29.58
15 ²	11.66	1.1085	150	29.68
20 ²	15.97	1.149	160	29.82
25 ²	21.88	1.2085	170	30.07
27.5 ²	25.15	1.241	180	30.26
30 ²	29.18	1.2795	190	30.46
32.38 ³	33.20	1.334	200	30.60
			210	30.65
-3.55 ^{4,5}	12.8	—	220	30.94
-1.25 ⁴	4.15	—	230	31.32
0 ⁶	15.11	—	233 ^{5,10}	31.7
5 ⁶	18.90	—	241 ¹⁰	31.88
10 ⁶	23.02	—	250	30.56
15 ⁶	27.11	—	260	29.48
20 ⁶	31.13	—	270	27.95
23.7 ⁷	34.38	—	280	26.04
24.25 ^{5,7}	34.3	—	290	23.55
			300	19.87
35 ⁸	32.93	1.329	300 ⁵	20.3
40 ⁸	32.48	1.3205	310	15.61
45 ⁸	32.07	1.3123	320	11.58
50 ⁸	31.69	1.3052	324.5 ⁵	10.0
60 ⁸	31.13	1.292	330	6.80
70 ⁸	30.65	1.280	340	4.03
80 ⁸	30.17	1.267	350	2.34
90 ⁸	29.87	1.2552	354 ⁵	1.62
100 ⁸	29.68	1.246	360	0.89
101.9 ⁹	29.68	1.2450	382	0.38

^aThe solid phases in equilibrium with these solutions are: 1, ice + Na₂SO₄·10H₂O; 2, Na₂SO₄·10H₂O; 3, Na₂SO₄·10H₂O + Na₂SO₄ (ortho); 4, ice + Na₂SO₄·10H₂O + Na₂SO₄·7H₂O (metastable); 5, data from Strakhov (1970); 6, Na₂SO₄·7H₂O (metastable); 7, Na₂SO₄ + Na₂SO₄·7H₂O (metastable); 23.47°C, Dyson (1962); 8, Na₂SO₄ (ortho) at temperatures from 32.38 to 233, 235 or 241°C; 9, boiling point; 10, Na₂SO₄ (ortho) + Na₂SO₄ (mono); mono alone at higher temps; 234.5 or 235°C; Dyson (1961).

been plotted for the second time in Fig. 7.2, but on a larger scale to better show this metastable heptahydrate field as well as the shape of the decahydrate and anhydrous sodium sulfate curves to 100°C.

Table 7.2 and Fig. 7.3 provide information on the solubility of sodium sulfate when the solution is also saturated with sodium chloride. Here the data from various authors

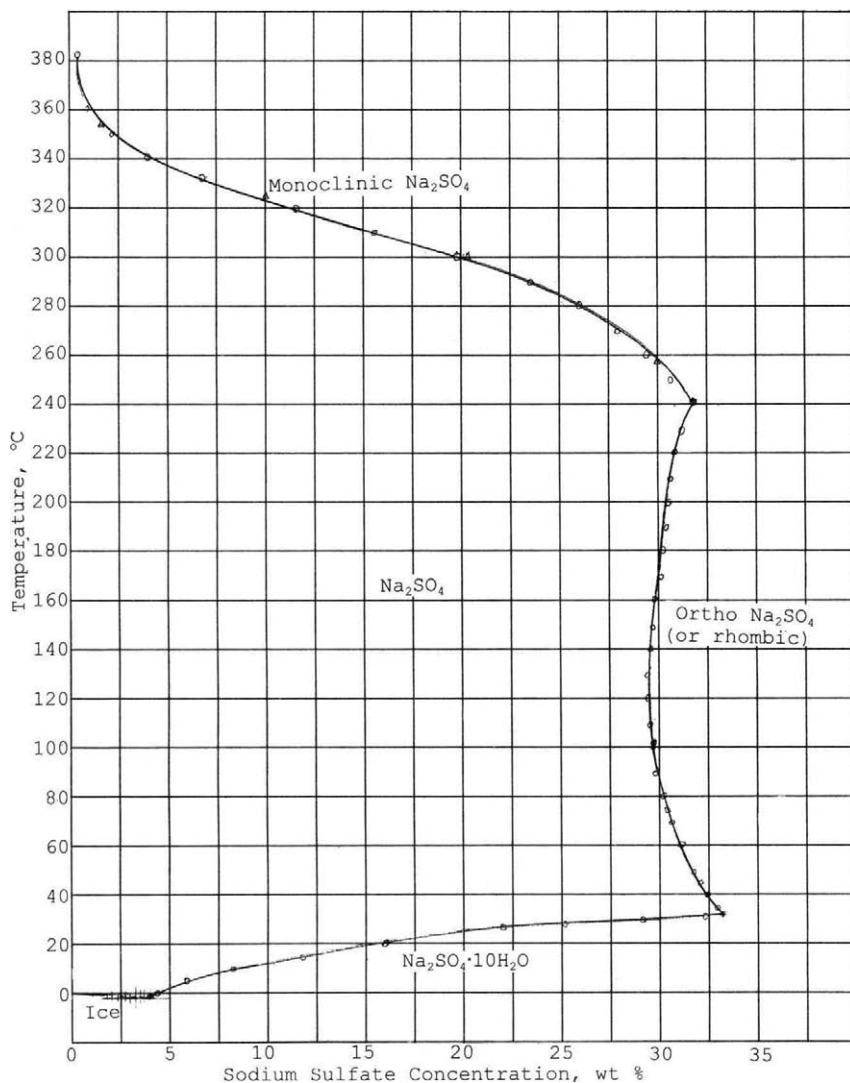


Figure 7.1 The solubility of sodium sulfate in water, 0–380°C (wt%).

is much less consistent, with that from Suhr (1937) perhaps being the most reliable. Again a consensus of the available numbers has been smoothed for the table and curves. The transition point from the decahydrate to anhydrous sodium sulfate in a saturated sodium chloride solution appears to be generally agreed upon at 17.9°C, but the corresponding concentration of sodium sulfate has been reported from 7.57% to

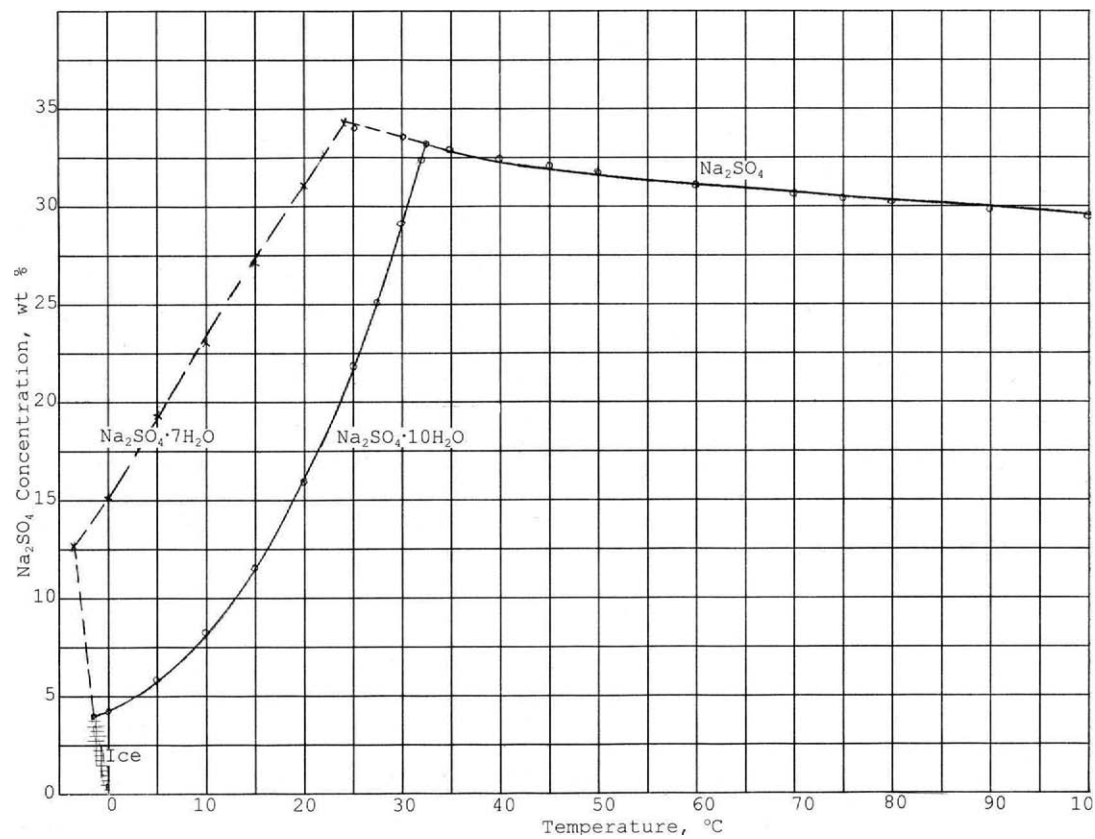


Figure 7.2 Solubility of sodium sulfate in water, expanded scale, 0–100°C (wt%).

Table 7.2

Solubility of Sodium Sulfate in Solutions Saturated with Sodium Chloride (wt%) (Seidell, 1965)^a

Temp. (°C)	NaCl	Na ₂ SO ₄	Density	Temp. (°C)	NaCl	Na ₂ SO ₄	Density
-10 ¹	24.53	0.43	—	40	23.66	5.86	1.228
-5 ¹	25.13	0.71	—	45	23.89	5.59	1.223
-0.1 ²	25.78	1.31	—	50	24.13	5.37	1.222
0 ³	25.79	1.32	—	55	24.38	5.16	1.220
5	25.3	2.3	1.213	60	24.64	5.02	1.218
10	24.45	3.53	1.223	65	24.9	4.9	1.214
15	23.23 ^b	5.52	1.236	70	25.12	4.8	1.210
17.5	22.45	7.31	1.247	75	25.3	4.78	1.207
17.9 ⁴	22.20 ^b	7.65 ^b	1.249	80	25.4	4.7	1.203
20	22.42 ^b	7.36 ^b	1.246	85	25.6	4.65	1.202
25	22.78 ^b	6.89 ^b	1.241	90	25.7	4.6	1.200
30	23.13	6.43 ^b	1.236	95	25.81	4.5	1.198
35	23.4	6.12	1.233	100	25.9	4.44	1.194
38	23.60	5.97	1.229	109.1 ^c	26.1	4.34	—

^aThe solid phases in equilibrium with the solutions are: 1, NaCl·2H₂O + Na₂SO₄·10H₂O; 2, NaCl + NaCl·2H₂O + Na₂SO₄·10H₂O; 3, NaCl + Na₂SO₄·10H₂O; 4, NaCl + Na₂SO₄ + Na₂SO₄·10H₂O.

^bSuhr (1937).

^cBoiling point.

7.70%. Suhr's value of 7.65% is considered to be the most correct and is near to the average of the other numbers. The corresponding sodium chloride concentration is 22.20%. Table 7.3 and Fig. 7.4 show the solubility of sodium sulfate with variable sodium chloride concentrations at several temperatures (10, 15, 25, and 100°C).

Table 7.4 lists the solubility and Janecke data for the reciprocal salt pair $\text{MgSO}_4 + 2\text{NaCl} \rightleftharpoons \text{Na}_2\text{SO}_4 + \text{MgCl}_2$ at 0, 20, 55, and 105°C. Figures 7.5 to 7.8 plot this data as the mole percent of the total salts present in the solution for each point on the Janecke diagrams. The square Janecke plots may be considered as back-to-back triangular diagrams with the values read as the normal two-coordinate numbers for the end components of each triangle, and the opposite component then equal to 100 minus the sum of the other two numbers. If only two components are listed (as in the Baabor, 1971, data), the center component may be shown as a hypothetical negative value if the total of the two listed salts is greater than 100%. The real numbers can be read after plotting the point and then considering a different triangular set with positive coordinates for the point. Also, with the Baabor data concentrations are not given, and only mole percents are listed in Table 7.4. To obtain each salt's concentration, the moles of water per total moles of salts must be divided into 1000, and that number multiplied by each of the percentages to give moles per 1000 moles of water.

These diagrams allow a prediction of the stable phases at any solution concentration and temperature, and for any point the solution's concentrations can be extrapolated from the data in Table 7.4. Similar data for several other temperatures have been reported

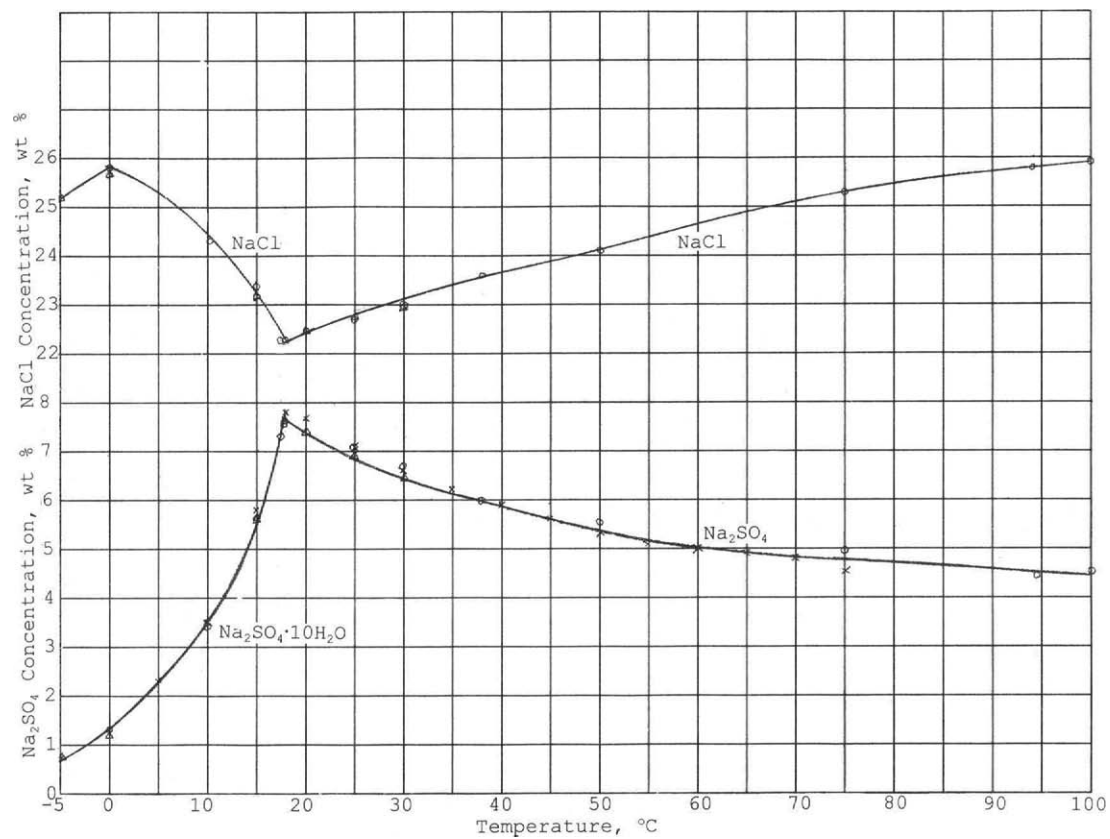


Figure 7.3 Solubility of sodium sulfate and sodium chloride in water when saturated with both salts, -5 to 100°C (wt%).

Table 7.3
Solubility Data for Mixed Sodium Sulfate–Sodium Chloride Solutions (wt%) (Seidell, 1965)^a

NaCl	Na ₂ SO ₄	Density	NaCl	Na ₂ SO ₄	Density
10°C			30°C		
0	8.37 ¹	1.080	0	29.1 ¹	1.280
3.87	5.80	1.083	1.74	27.19	1.282
8.39	4.16	1.102	3.35	26.0	1.283
8.78	4.07	1.102	3.95	25.68	1.284
13.08	3.34	1.150	5.50	24.99	1.290
17.2	3.26	1.159	5.68	25.0 ³	1.291
17.35	3.16	1.164	7.46	22.24	1.276
21.27	3.14	1.192	8.69	21.00	1.270
22.39	3.23	1.207	11.13	17.79	1.258
23.58	3.35	1.217	12.2	16.2	—
24.45	3.53 ²	1.224	13.20	15.24	1.249
26.32	0	—	14.79	13.64	1.244
15°C			18.0	9.70	—
0	11.5 ¹	1.109	23.0	6.68 ⁴	1.237
5.42	7.86	—	26.51	0	—
11.51	5.87	—	50°C		
15.97	5.23	—	0	31.6 ⁵	1.305
21.03	5.26	—	7.85	20.8	1.247
23.23	5.52 ²	1.236	16.1	11.3	1.216
25.21	2.26	—	24.1	5.54 ⁴	1.223
26.35	0	—	25.4	2.56	1.203
25°C			26.86	0	—
0	21.8 ¹	1.209	75°C		
2.28	20.53	1.2173	0	30.5 ⁵	1.274
4.45	18.69	1.2162	7.76	19.7	—
7.54	16.3	1.2150	16.5	10.2	—
7.66	16.0	1.217	25.3	4.95 ⁴	1.207
10.09	14.75	1.2275	26.4	2.14	1.189
11.68	14.50	1.2385	27.4	0	—
13.68	14.82 ³	1.2571	100°C		
16.65	11.67	1.2476	0	29.6 ⁵	1.246
18.4	10.4	1.239	7.67	18.6	—
19.07	9.08	1.2429	18.4	8.75	—
22.02	7.08	1.2438	25.9	4.51 ⁴	1.194
22.78	6.89 ⁴	1.2451	27.2	1.84	1.777
24.07	4.74	1.2309	28.15	0	—
24.6	3.35	1.216			
25.08	2.45	1.2162			
26.36	0	1.2002			

^aThe solid phases in equilibrium with the solutions are: 1, Na₂SO₄·10H₂O; 2, Na₂SO₄·10H₂O and NaCl; 3, Na₂SO₄·10H₂O and Na₂SO₄; 4, Na₂SO₄ and NaCl; 5, Na₂SO₄.

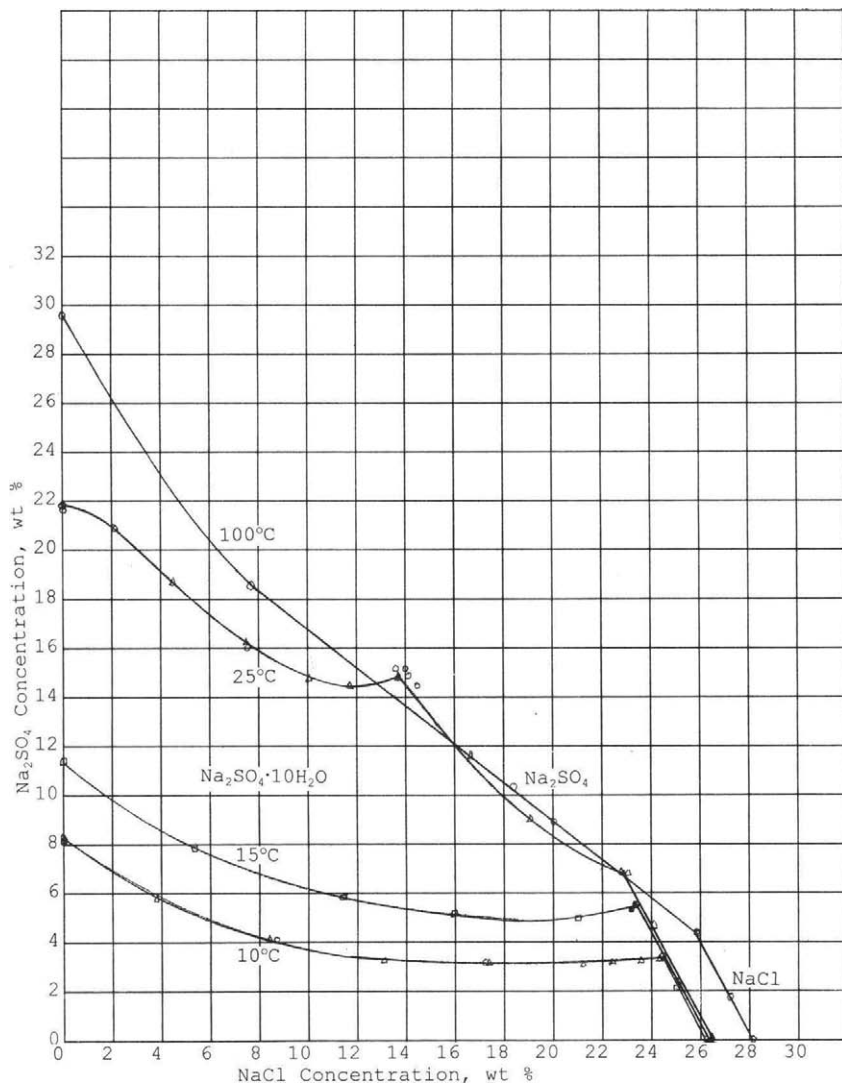


Figure 7.4 The solubility of sodium sulfate and sodium chloride mixtures in water at 10, 15, 25, and 100°C (wt%).

by the authors listed. In this system the kinetics for the crystallization of most of the double salts is very slow, and it takes even more time to reach the equilibrium conditions shown in the table and figures. Consequently, any study of this reciprocal salt pair for possible industrial use finds that the actual concentration paths (and even some of the phases involved) will vary widely from that predicted by this data.

The convoluted shapes of the double salt fields in Figs. 7.6 and 7.7, and the different results from different investigators shown in the tables, are evidence of this difficulty in obtaining true equilibrium in this system (in Fig. 7.8 the regular shapes are merely a result of limited data).

Table 7.4
Phase Data on the Reciprocal Salt Pair
 $\text{MgSO}_4 + 2\text{NaCl} \rightleftharpoons \text{Na}_2\text{SO}_4 + \text{MgCl}_2$ (Baabor, 1971)^a

MgCl ₂		MgSO ₄		Na ₂ Cl ₂		Na ₂ SO ₄		m ^d	Solid phases ^f
Conc. ^b	% ^c	Conc. ^b	% ^c	Conc. ^b	% ^c	Conc. ^b	% ^c		
0°C									
—	0	—	—	—	—	—	4.30	18.00	C2 + S10
—	1.87	—	—	—	—	—	3.99	17.70	C0 + S10
—	3.69	—	—	—	—	—	3.74	17.83	C0 + S10
—	9.83	—	—	—	—	—	4.12	17.72	C0 + S10
—	19.00	—	—	—	—	—	4.95	17.75	C0 + S10
—	29.50	—	—	—	—	—	7.94	17.45	C0 + S10
—	38.40	—	—	—	—	—	8.80	17.28	C0 + S10
—	41.30	—	—	—	—	—	9.06	17.22	C0 + S10
—	52.00	—	—	—	—	—	14.03	16.46	C0 + S10
—	59.62	—	—	—	—	—	18.93	16.14	C0 + S10 + Mg7
25.2 ^e	40.32	12.0	19.20	25.3	40.48	—	—	—	C0 + S10 + Mg7
—	71.52	—	—	—	—	—	13.41	15.90	C0 + Mg7
48.2 ^e	73.93	6.0	9.20	11.0	16.87	—	—	—	C0 + Mg7
—	77.50	—	—	—	—	—	11.31	15.87	C0 + Mg7
—	81.40	—	—	—	—	—	10.03	15.46	C0 + Mg7
—	86.43	—	—	—	—	—	8.41	15.17	C0 + Mg7
—	89.40	—	—	—	—	—	7.17	14.60	C0 + Mg7
—	93.18	—	—	—	—	—	5.83	14.07	C0 + Mg7
—	95.60	—	—	—	—	—	4.80	13.33	C0 + Mg7
85.7 ^e	95.64	2.9	3.24	1.0	1.12	—	—	—	C0 + Mg7
—	97.11	—	—	—	—	—	4.23	12.49	C0 + Mg7
—	99.38	—	—	—	—	—	3.64	9.88	C0 + Mg7 + MgC6
96.5 ^e	95.08	3.9	3.84	1.1	1.08	—	—	—	C0 + Mg7 + MgC6
—	98.69	—	—	—	—	—	0.00	9.87	C0 + MgC6
—	100.00	—	—	—	—	—	3.48	9.77	Mg7 + MgC6
—	68.40	—	—	—	—	—	25.40	18.56	Mg7 + S10
—	74.45	—	—	—	—	—	41.25	20.82	Mg7 + S10
—	77.75	—	—	—	—	—	57.25	22.15	Mg7 + S10
—	80.90	—	—	—	—	—	74.95	22.50	Mg7 + S10
—	81.73	—	—	—	—	—	89.57	22.02	Mg7 + S10
23.7 ^e	42.17	13.3	23.67	19.2	34.16	—	—	—	Mg7 + S10
11.0 ^e	24.72	23.8	53.48	9.7	21.80	—	—	—	Mg7 + S10
—	83.39	—	—	—	—	—	100.00	21.67	Mg7 + S10
— ^e	—	38.5	85.56	—	—	6.5	14.44	—	Mg7 + S10

(continues)

Table 7.4
(continued)

MgCl ₂		MgSO ₄		Na ₂ Cl ₂		Na ₂ SO ₄		m ^d	Solid phases ^f
Conc. ^b	% ^c	Conc. ^b	% ^c	Conc. ^b	% ^c	Conc. ^b	% ^c		
20°C									
— ^h	—	—	—	55.18	100	—	—	—	CO
103.2 ^h	100	—	—	—	—	—	—	—	MgC6
— ^h	—	53.55	100	—	—	—	—	—	Mg7
— ^h	—	—	—	—	—	25.58	100	—	S10
—	0.00	—	—	—	—	—	27.00	16.36	S0 + S10
—	7.86	—	—	—	—	—	31.15	16.33	S0 + S10
—	14.81	—	—	—	—	—	34.90	16.37	S0 + S10
—	25.35	—	—	—	—	—	43.55	15.65	S0 + S10
—	26.05	—	—	—	—	—	43.00	16.07	S0 + S10 + A
—	0.00	—	—	—	—	—	21.30	15.95	S0 + C0
— ^h	—	—	—	49.5	78.82	13.3	21.18	—	S0 + C0
—	7.90	—	—	—	—	—	22.75	15.92	S0 + C0
—	14.54	—	—	—	—	—	25.15	16.00	S0 + C0
—	20.50	—	—	—	—	—	26.90	15.63	S0 + C0
—	24.20	—	—	—	—	—	29.90	15.17	S0 + C0 + A
—	25.75	—	—	—	—	—	28.70	15.90	C0 + A
—	29.95	—	—	—	—	—	27.55	15.63	C0 + A
—	38.25	—	—	—	—	—	25.08	16.12	C0 + A
—	41.60	—	—	—	—	—	24.70	16.00	C0 + A
—	45.10	—	—	—	—	—	25.20	15.70	C0 + A
—	48.40	—	—	—	—	—	25.30	15.47	C0 + A
—	53.00	—	—	—	—	—	24.25	15.68	C0 + A
—	57.50	—	—	—	—	—	23.05	15.82	C0 + A
—	60.00	—	—	—	—	—	24.10	15.32	C0 + A
—	64.10	—	—	—	—	—	23.32	15.43	C0 + A
—	67.60	—	—	—	—	—	22.42	15.41	C0 + A
—	75.80	—	—	—	—	—	23.60	14.72	C0 + A + Mg7
40.31 ^h	55.2	14.25	19.51	18.47	25.29	—	—	—	C0 + A + Mg7
—	83.48	—	—	—	—	—	18.94	14.21	C0 + Mg7
62.05 ^g	79.61	10.0	12.83	5.89	7.56	—	—	—	C0 + Mg7
80.38 ^h	87.51	9.71	10.57	1.68	1.92	—	—	—	C0 + Mg7
—	91.20	—	—	—	—	—	14.27	13.32	C0 + Mg7
—	96.19	—	—	—	—	—	10.62	12.12	C0 + Mg7
—	96.99	—	—	—	—	—	9.38	11.55	C0 + Mg7 + Mg6
76.6 ^g	87.57	8.57	9.72	2.37	2.61	—	—	—	C0 + Mg7 + Mg6
80.2 ^h	84.42	8.8	9.26	6.0	6.32	—	—	—	C0 + Mg7 + Mg6
—	99.45	—	—	—	—	—	7.76	10.31	C0 + Mg5 + Mg6
—	99.61	—	—	—	—	—	4.98	9.49	C0 + Mg5 + MgC6
—	99.57	—	—	—	—	—	3.29	9.63	C0 + MgC6

(continues)

Table 7.4
(continued)

MgCl ₂		MgSO ₄		Na ₂ Cl ₂		Na ₂ SO ₄		m ^d	Solid phases ^f
Conc. ^b	% ^c	Conc. ^b	% ^c	Conc. ^b	% ^c	Conc. ^b	% ^c		
20°C									
77.78 ^e	88.28	8.3	9.42	2.03	2.30	—	—	—	C0 + MgC6
—	99.73	—	—	—	—	—	3.13	9.73	C0 + MgC6
—	99.03	—	—	—	—	—	0.99	9.74	C0 + MgC6
—	98.58	—	—	—	—	—	0.00	9.70	C0 + MgC6
—	99.09	—	—	—	—	—	10.00	11.30	Mg7 + Mg6
—	100.00	—	—	—	—	—	10.75	11.19	Mg7 + Mg6
—	100.00	—	—	—	—	—	7.61	10.18	Mg5 + Mg6
—	100.00	—	—	—	—	—	4.56	9.57	Mg5 + MgC6
—	75.00	—	—	—	—	—	26.00	15.50	Mg7 + A
—	71.55	—	—	—	—	—	35.90	16.20	Mg7 + A
—	66.75	—	—	—	—	—	49.90	16.02	Mg7 + A
—	65.90	—	—	—	—	—	56.50	16.02	Mg7 + A
—	66.10	—	—	—	—	—	63.10	16.12	Mg7 + A
—	64.40	—	—	—	—	—	69.45	15.67	Mg7 + A
—	63.90	—	—	—	—	—	75.70	15.57	Mg7 + A
—	61.80	—	—	—	—	—	81.50	15.22	Mg7 + A
—	60.40	—	—	—	—	—	83.50	15.15	Mg7 + A
—	59.20	—	—	—	—	—	84.70	14.23	Mg7 + A
—	58.70	—	—	—	—	—	85.34	14.37	Mg7 + A
—	57.70	—	—	—	—	—	85.78	14.06	Mg7 + A + S10
— ^h	—	41.95	61.20	—	—	26.6	38.80	—	Mg7 + A + S10
—	59.15	—	—	—	—	—	87.88	14.47	Mg7 + S10
—	60.65	—	—	—	—	—	89.78	14.50	Mg7 + S10
—	61.00	—	—	—	—	—	91.15	14.30	Mg7 + S10
—	61.60	—	—	—	—	—	91.40	14.60	Mg7 + S10
—	61.50	—	—	—	—	—	92.37	14.46	Mg7 + S10
—	62.50	—	—	—	—	—	95.75	14.40	Mg7 + S10
—	66.90	—	—	—	—	—	100.00	14.84	Mg7 + S10
—	61.50	—	—	—	—	—	76.10	15.84	A + S10
—	43.00	—	—	—	—	—	62.50	15.90	A + S10
—	41.00	—	—	—	—	—	59.30	15.55	A + S10
—	34.75	—	—	—	—	—	52.50	15.73	A + S10
—	32.50	—	—	—	—	—	51.50	15.67	A + S10
—	29.05	—	—	—	—	—	47.90	15.67	A + S10
—	26.70	—	—	—	—	—	43.80	15.60	A + S10
—	25.85	—	—	—	—	—	40.70	16.00	A + S0
—	24.95	—	—	—	—	—	36.95	15.80	A + S0
—	24.58	—	—	—	—	—	33.20	15.52	A + S0
—	24.05	—	—	—	—	—	31.70	15.30	A + S0

(continues)

Table 7.4
(continued)

MgCl ₂		MgSO ₄		Na ₂ Cl ₂		Na ₂ SO ₄		Density	Phases ^f
Conc. ⁱ	% ^c	Conc. ⁱ	% ^c	Conc. ⁱ	% ^c	Conc. ⁱ	% ^c		
55°C ^e									
—	—	34.40	100.0	—	—	—	—	—	Mg6
—	—	33.66	88.09	—	—	5.37	11.91	1.440	Mg6 + A
—	—	12.93	39.38	—	—	23.49	60.62	1.404	A + S
—	—	—	—	—	—	31.56	100.0	1.298	S
—	—	—	—	24.36	91.98	5.16	8.02	1.234	S + Na
—	—	—	—	26.92	100.0	—	—	—	Na
36.56	89.05	—	—	2.76	10.95	—	—	—	Na + MgC6
37.60	100.0	—	—	—	—	—	—	—	MgC6
37.33	99.08	0.44	0.92	—	—	—	—	1.359	MgC6 + Mg1
14.90	51.01	18.09	48.49	—	—	—	—	1.350	Mg6 + Mg1
—	—	12.18	31.90	5.61	30.26	17.05	37.84	—	L + A
—	—	10.89	26.65	9.28	46.77	12.82	26.58	1.327	S + A + V
—	—	10.09	23.19	12.60	59.64	8.82	17.17	—	S + V
—	—	9.42	21.15	13.69	63.32	8.16	15.53	—	S + V
—	—	9.95	20.16	17.74	74.02	3.39	5.82	—	S + V
1.14	2.67	7.97	14.79	21.60	82.54	—	—	1.266	S + V + Na
—	—	4.21	7.65	23.89	89.19	2.07	3.18	—	S + Na
—	—	3.17	5.77	24.04	90.04	2.72	4.19	—	S + Na
2.51	6.03	7.82	14.86	20.21	79.11	—	—	—	V + Na
4.97	12.53	7.63	15.22	17.59	72.25	—	—	1.291	V + Na
6.35	16.21	7.69	15.53	16.41	68.26	—	—	—	V + Na
9.74	26.38	7.87	16.86	12.86	56.76	—	—	—	V + Na
12.92	37.66	7.62	17.57	9.43	44.77	—	—	—	V + Na
13.64	39.36	8.24	18.81	8.90	41.83	—	—	1.314	V + Na + L
10.60	31.74	16.32	38.65	6.07	29.61	—	—	—	A + L
8.54	26.16	22.42	54.33	3.91	19.51	—	—	—	A + L
7.51	23.21	23.73	58.01	3.73	18.78	—	—	—	A + L
7.32	22.73	24.95	61.28	3.16	15.99	—	—	1.383	A + L + Mg6
5.21	15.76	26.73	63.94	4.12	20.30	—	—	—	A + Mg6
0.35	1.05	33.51	79.34	4.02	19.61	—	—	—	A + Mg6
10.80	34.46	21.65	54.63	2.10	10.91	—	—	1.351	L + Mg6
13.24	42.37	19.95	50.49	1.37	7.14	—	—	—	L + Mg6
14.36	45.93	19.02	48.13	1.14	5.94	—	—	1.337	L + Mg6 + Mg1
15.47	48.47	17.15	42.50	1.77	9.03	—	—	—	L + Mg1
17.70	55.30	15.00	37.07	1.50	7.63	—	—	—	L + Mg1
18.41	56.94	14.41	35.25	1.55	7.81	—	—	—	L + Mg1
24.24	72.15	7.38	17.38	2.16	10.47	—	—	1.317	L + Mg1 + Na
32.74	88.69	2.81	6.02	1.20	5.29	—	—	—	Mg1 + Na
37.52	97.91	0.40	0.82	0.30	1.27	—	—	1.363	Mg1 + Na + MgC6

(continues)

Table 7.4
(continued)

MgCl ₂		MgSO ₄		Na ₂ Cl ₂		Na ₂ SO ₄		Solid phases ^f
Conc. ^b	% ^c	Conc. ^b	% ^c	Conc. ^b	% ^c	Conc. ^b	% ^c	
105°C ^e								
139.5	100.0	—	—	—	—	—	—	MgC6
133.0	99.83	—	—	0.23	0.17	—	—	MgC6 + Na
138.5	98.93	1.5	1.07	—	—	—	—	MgC6 + Mg1
123.1	98.33	2.09	1.67	—	—	—	—	MgC6 + Mg1
—	—	76.69	100.0	—	—	—	—	Mg1
—	—	64.31	83.11	—	—	13.07	16.89	Mg1 + 2·2·5
—	—	41.84	56.49	—	—	32.22	43.51	1·1 + 2·2·5
—	—	49.88	81.86	—	—	11.05	18.14	1·1 + S
—	—	—	—	—	—	52.99	100.0	S
—	—	—	—	57.99	87.81	8.05	12.19	S + Na
4.63	7.15	—	—	52.78	81.46	7.38	11.39	S + Na + 3·1
33.64	47.53	—	—	27.02	38.17	10.12	14.30	2·2·5 + Na + 3·1
55.40	72.23	—	—	9.98	13.01	11.32	14.76	2·2·5 + Na + Mg1

^aThe NaCl-saturated data from Autenrieth and Braune (1960) are very similar.^bConcentration in moles per 1000 moles of water.^cValues for the phase diagram as the mole percent of the total moles present.^dThe moles of water per mole of the total salts present.^eData from Seidell (1965).

^fCO or Na = NaCl; C2 = NaCl·2H₂O; SO or S = Na₂SO₄; S10 = Na₂SO₄·10H₂O; Mg1 = MgSO₄·H₂O (kieserite); Mg5 = MgSO₄·5H₂O; Mg6 = MgSO₄·6H₂O; Mg7 = MgSO₄·7H₂O; MgC6 = MgCl₂·6H₂O; A = 1:1:4 = astrakanite (NaSO₄·MgSO₄·4H₂O); L = 2:2:5 = loewite (2Na₂SO₄·2MgSO₄·5H₂O); V = 3:1 = vanthoffite (3Na₂SO₄·MgSO₄), 1:1 = Na₂SO₄·MgSO₄.

^gData from Autenrieth and Braune (1960).^hData from Rovera (1960) at 20.6°C.ⁱConcentration in weight percent.

With the appropriate solution concentrations, and at equilibrium, astrakanite (Na₂SO₄·MgSO₄·4H₂O) may first appear as a stable phase only above 5–10°C and anhydrous sodium sulfate at 17.9°C; sodium sulfate decahydrate disappears between 25 and 30°C; epsomite (MgSO₄·7H₂O) changes to the hexa and monohydrates (kieserite) between 30 and 50°C; vanthoffite (3Na₂SO₄·MgSO₄) and loewite (2Na₂SO₄·2MgSO₄·5H₂O) appear between 50 and 55°C; magnesium sulfate hexahydrate disappears at about 60°C; loewite vanishes by about 70°C; and astrakanite disappears somewhat above 110°C.

Additional data on this system has been presented by several other authors, including Amirkhanov (1964), Artykova and Kashkarov (1983; at 35°C), Bochkareva (1968), Kurnokow and Zemczunzy (1924), and Zdanovskii (1979; also Zdanovskii and Afonichkin, 1976). Typical of the literature on this system where calcium is also

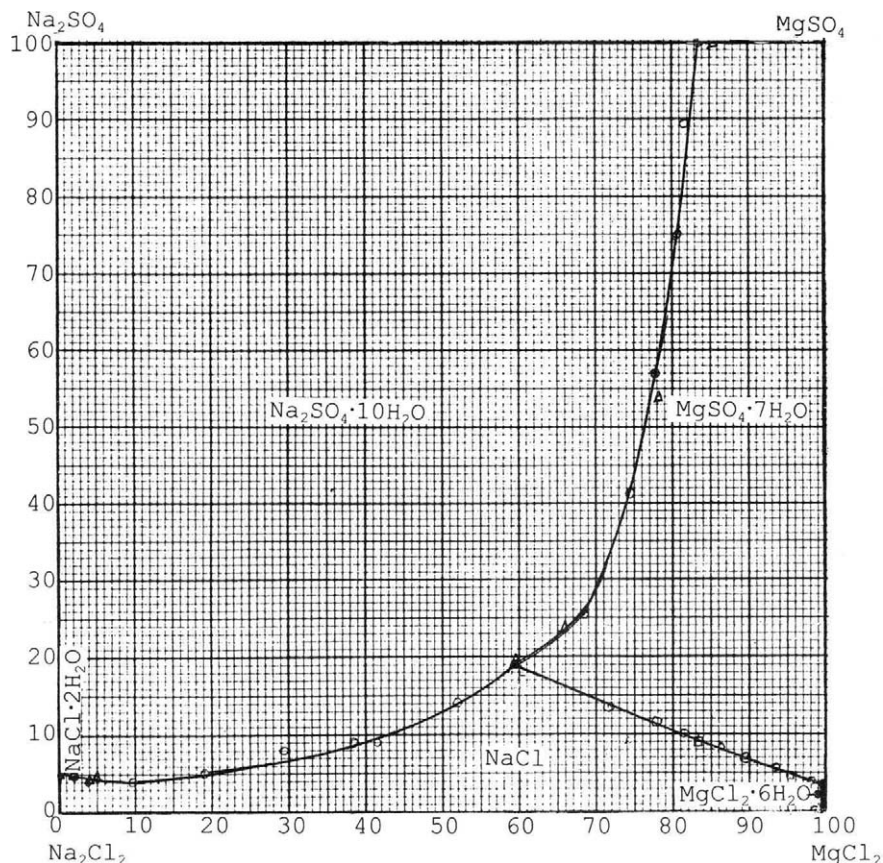


Figure 7.5 The $\text{MgSO}_4 + 2\text{NaCl} \rightleftharpoons \text{Na}_2\text{SO}_4 + \text{MgCl}_2$ Janecke phase diagram at 0°C (mol% of the salts present).

present are the articles by Ryspaev (1975) and co-workers (1978, 1975). There is an even more extensive literature on the seawater system where both calcium and potassium are also present.

Table 7.5 and Fig. 7.9 present data on the simple system of sodium sulfate with magnesium sulfate. In this system (according to Froelich, 1929), astrakanite first becomes stable between 21 and 26°C . It is replaced by loewite between 61 and 70°C , and the loweite disappears at 190°C . Vanthoffite first forms at about 60°C , and mirabilite is replaced by thenardite between 26 and 32.4°C . Magnesium sulfate dodecahydrate is stable below 0 – 2°C , and epsomite from there to 46 – 49°C . It is replaced by magnesium sulfate hexahydrate, which disappears between 62 and 68°C , while kieserite (the monohydrate) is stable from there to higher temperatures. The

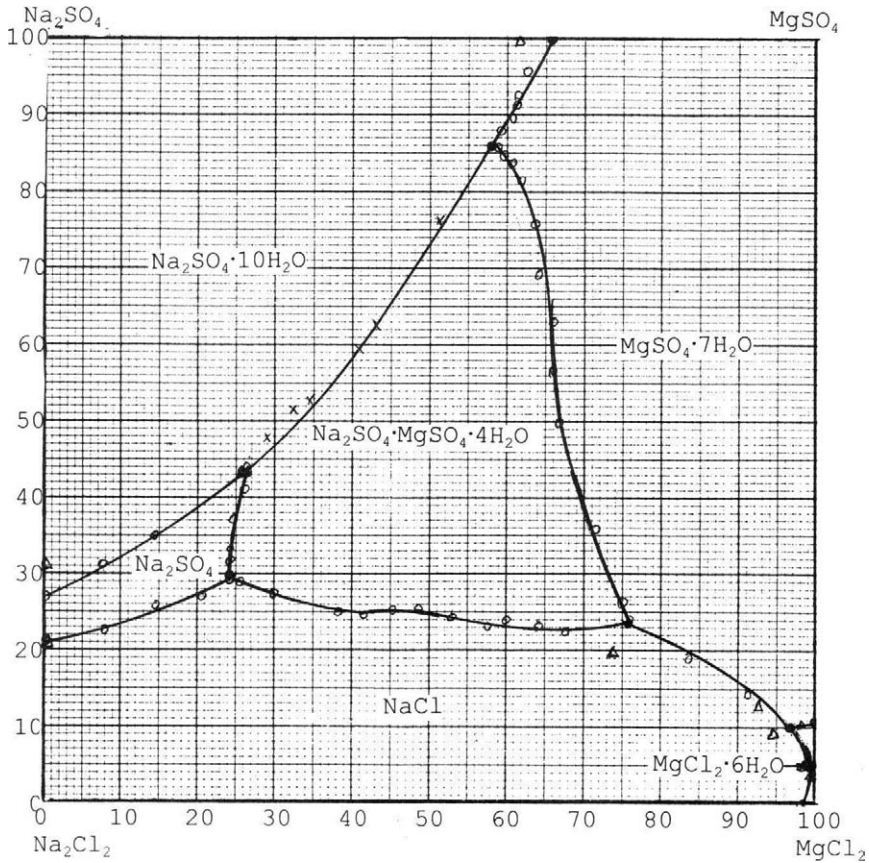


Figure 7.6 The $\text{MgSO}_4 + 2\text{NaCl} \rightleftharpoons \text{Na}_2\text{SO}_4 + \text{MgCl}_2$ Janecke phase diagram at 20°C (mol% of the salts present).

thenardite field becomes very small and may also disappear at about 190°C. Additional data on the system in the presence of calcium has been presented by several authors, including Batyrchaev and Ryspaev (1972, 1971).

Table 7.6 and Fig. 7.10 present data on solutions saturated with both glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, or anhydrite [CaSO_4]; i.e., these solid phases are always in contact with the solution), with or without various amounts of sodium chloride also being present. With no NaCl present there is a 3–7% difference in the sodium sulfate concentration predicted by the two major investigators' data, so both sets have been listed. The small amount of data from Seidell (1965) is a compilation from earlier investigators and appears to agree most closely with that of Hill and Wills (1938), so perhaps it is the most accurate.

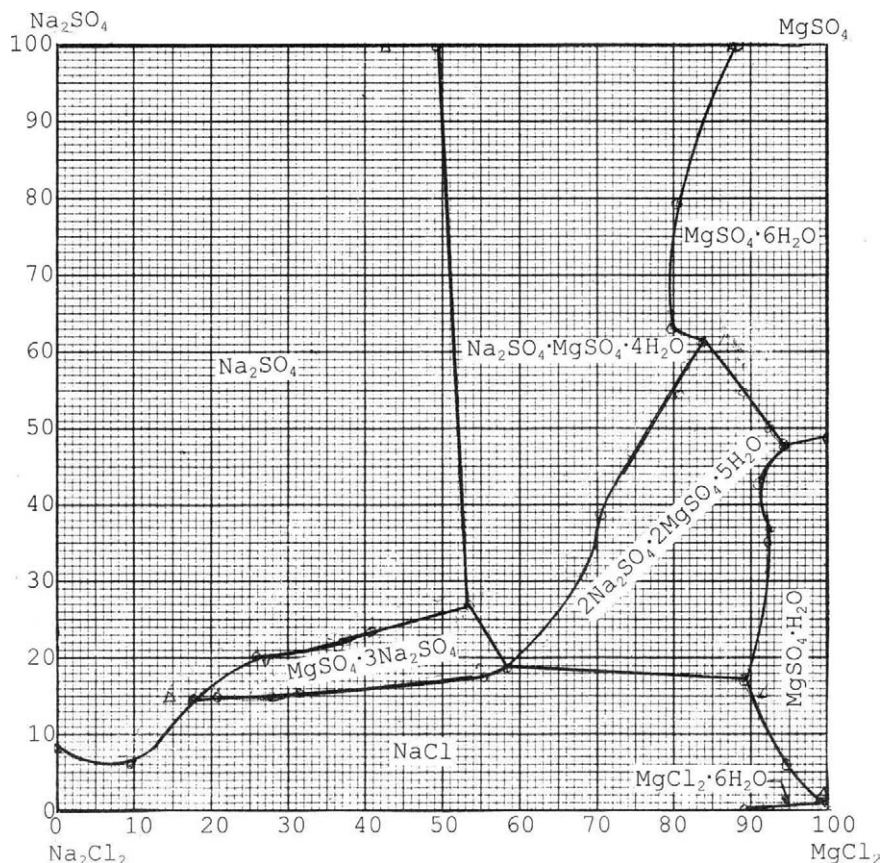


Figure 7.7 The $\text{MgSO}_4 + 2\text{NaCl} \rightleftharpoons \text{Na}_2\text{SO}_4 + \text{MgCl}_2$ Janecke phase diagram at 55°C (mol% of the salts present).

Also, Hill and Wills reached equilibrium starting with glauberite and water, whereas the others started with gypsum and thenardite. Beyond about 40°C if anhydrite is present (it is only stable above about 85°C with salt present, and >100°C without salt), Hill and Wills (1938) indicate slightly higher sodium sulfate, and lower calcium sulfate solubilities. Several other fragmentary studies have been made on this system (which do not help predict the glauberite solubility), including articles by Cortelezzi and Carrica (1965), Freyer *et al.* (1997), Kurilenko (1977), Moller (1988), Shuqui and Huanzhu (1989, 1986), and Susarla and Sanghavi (1993).

Table 7.7 and Fig. 7.11 provide data on the sodium sulfate–sodium carbonate system at several temperatures. There are a number of forms of burkeite

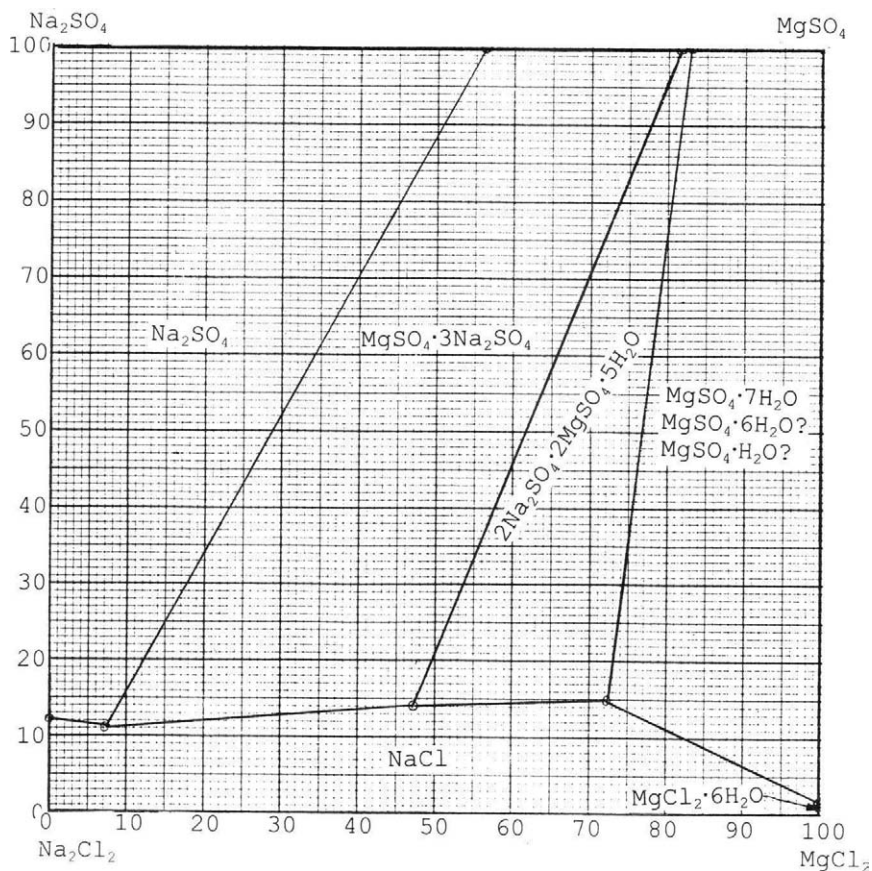


Figure 7.8 The $\text{MgSO}_4 + 2\text{NaCl} \rightleftharpoons \text{Na}_2\text{SO}_4 + \text{MgCl}_2$ Janecke phase diagram at 105°C (mol% of the salts present).

($\text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4$) at higher temperatures, so for convenience they have been merely listed as 1·2? (see the Searles Lake section for one example of the alternate burkeite forms). The declining solubility of both salts with the presence of the other is evident from Fig. 7.11. Other references on this system include that by Mehrotra (1989).

Phase data for the reciprocal salt pair $\text{Na}_2\text{SO}_4 + 2\text{KCl} \rightleftharpoons \text{K}_2\text{SO}_4 + 2\text{NaCl}$ at 25°C is listed in Table 7.8, and a Janecke diagram for the system is shown in Fig. 7.12. In this case the concentration units are listed as g/100 g H_2O , and the kinetics of reaching equilibrium are quite fast. This allows the diagram to be followed quite accurately for the industrial production of potassium sulfate from sodium sulfate and potash via the glaserite ($3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$) process.

Table 7.5
Phase Data for the System $\text{Na}_2\text{SO}_4\text{--MgSO}_4$ (wt%) (Seidell, 1965)

Dens.	MgSO ₄	Na ₂ SO ₄	Phase ^a	Dens.	MgSO ₄	Na ₂ SO ₄	Phase ^a
0°C				25°C (cont.)			
—	20.31	0.0	Mg7	—	10.93	19.17	Na10
—	20.0	4.3	Mg7	1.320	10.89	18.87	Na10
—	19.83	4.28	Mg7 + Na10	—	10.78	18.85	Na10
—	19.90 ^b	4.34	Mg7 + Na10	1.276	6.00	20.42	Na10
—	11.25	4.69	Na10	1.251	3.73	20.79	Na10
—	9.65	4.89	Na10	—	3.34	20.88	Na10
1.041	0.0	4.2	Na10	—	3.34	20.88	Na10
15°C				1.209	0.0	21.77	Na10
50°C				50°C			
1.204	25.13	0.0	Mg7	1.401	33.50	0.0	Mg6
—	24.92	0.26	Mg7	1.410	32.50	1.96	Mg6
1.291	24.75	0.75	Mg7	1.426	31.60	3.95	Mg6
1.292	24.33	1.68	Mg7	1.428	31.32	4.74	Mg6 + 1·1·4
1.286	23.81	3.97	Mg7	1.414	27.49	7.55	1·1·4
1.301	22.29	7.88	Mg7	1.380	20.16	13.86	1·1·4
—	21.59	10.93	Mg7	—	18.2	16.0	1·1·4
1.319	20.88	11.72	Mg7 + Na10	—	16.0	18.3	1·1·4
1.271	13.89	9.92	Na10	1.374	15.75	18.62	1·1·4
—	8.09	9.90	Na10	1.381	11.98	23.25	1·1·4 + Na10
1.185	3.63	10.07	Na10	1.364	9.80	24.77	Na10
1.132	1.21	10.92	Na10	1.329	3.52	29.42	Na10
1.109	0.0	11.5	Na10	—	2.6	30.0	Na10
25°C				1.305	0.0	31.70	Na10
80°C				80°C			
1.304	26.68	0.0	Mg7	—	38.6	0.0	Mg1
1.320	25.66	2.42	Mg7	—	38.4	2.8	Mg1
—	25.48	2.73	Mg7	—	36.3	4.9	2·2·5
—	24.94	3.54	Mg7	—	33.25	6.35	2·2·5
—	24.49	5.29	Mg7	—	24.06	12.6	2·2·5
1.364	23.53	7.96	Mg7	—	18.1	17.85	2·2·5
—	23.49	7.50	Mg7	—	16.4	19.7	2·2·5
—	22.32	10.10	Mg7	—	15.4	21.4	2·2·5
—	22.2	10.8	Mg7	—	14.7	22.0	2·2·5
1.389	21.39	12.40	Mg7 + 1·1·4	—	14.55	22.3	2·2·5 + 1·3
—	21.35 ^b	12.35	Mg7 + 1·1·4	—	14.2	22.25	1·3
1.383	18.33	15.70	1·1·4	—	13.85	22.55	1·3
—	18.28	15.89	1·1·4	—	4.29	28.1	1·3 + S
—	16.31	18.22	1·1·4	1.267	0.0	30.35	S
—	16.14	18.16	1·1·4				
1.384	15.6	18.5	1·1·4 + Na10				
—	15.76 ²	18.55	1·1·4 + Na10				

^aMg7 = $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (epsomite), Na10 = $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (mirabilite), 1·1·4 = $\text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ (astrakanite), Mg1 = $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ (kieserite), 1·3 = $\text{MgSO}_4 \cdot 3\text{Na}_2\text{SO}_4$ (vanthoffite), 2·2·5 = $2\text{MgSO}_4 \cdot 2\text{Na}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$ (loweite), S = Na_2SO_4 (thenardite).

^bData from Froelich (1929).

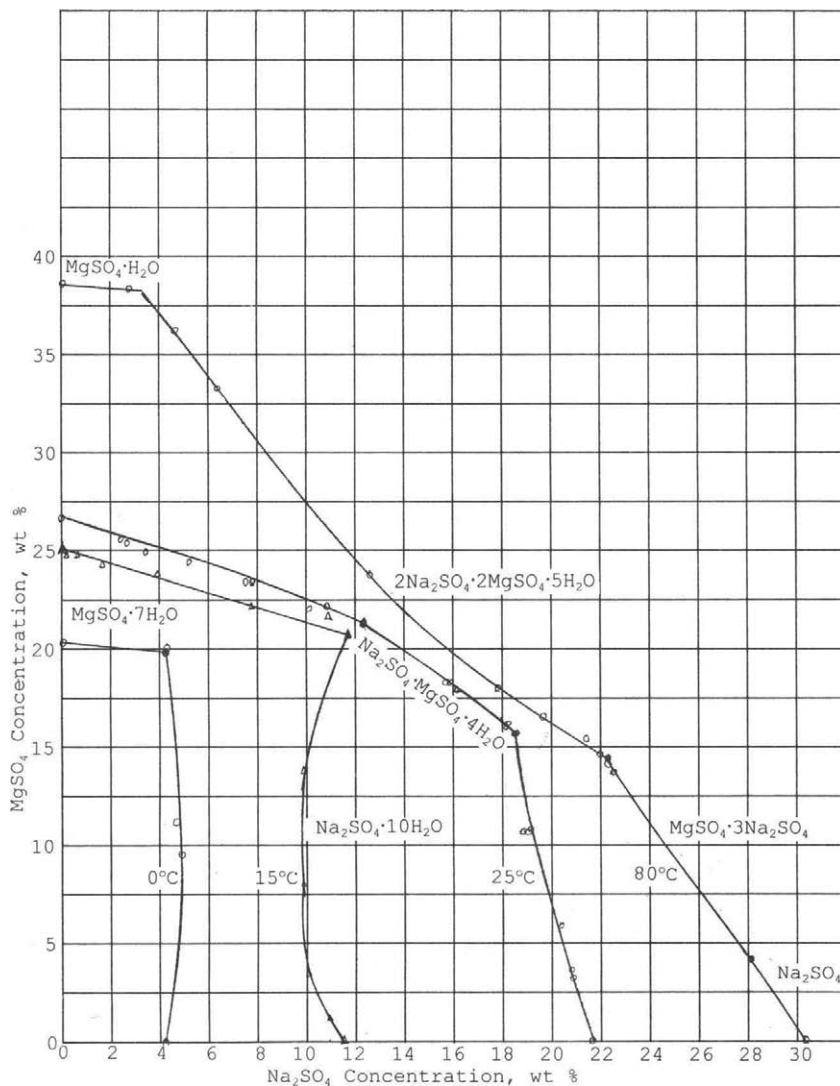


Figure 7.9 The solubility of sodium sulfate and magnesium sulfate mixtures in water at 0, 15, 25, and 80°C (wt%).

PHYSICAL PROPERTIES

The density of saturated sodium sulfate and sodium sulfate–sodium chloride solutions from 0 to 100°C is shown in Fig. 7.13 and listed in Tables 7.1 and 7.2. The densities of saturated solutions of sodium sulfate–sodium chloride are given in

Table 7.6
Sodium Sulfate and Calcium Sulfate Solubility when Glauberite and
Gypsum or Anhydrite are Present (wt%) (Block and Walters, 1968)

		Temp. (°C)					
		25 ^a	40	55	70	85	100
No NaCl	Na ₂ SO ₄	21.32	23.05	18.39	15.09	15.94	17.51
	CaSO ₄	0.198	0.208	0.209	0.221	0.154	0.105

		Temp. (°C)						
		23.2 ^a	25 ^a	27.2 ^a	35	50	60	75
No NaCl	Na ₂ SO ₄	20.0 ^b	21.8 ^b	25.1 ^b	22.9 ^b	18.7 ^b	16.3 ^b	13.9 ^b
	Na ₂ SO ₄	—	21.75 ^c	—	22.65 ^c	18.71 ^c	—	—
	CaSO ₄	—	0.197 ^{b,c}	—	0.206 ^c	0.227 ^c	—	—

		Temp. (°C)					
		25 ^a	40	55	70	85	100
0.5 M NaCl	Na ₂ SO ₄	20.14	18.23	15.75	12.06	12.77	14.44
	CaSO ₄	0.178	0.172	0.204	0.195	0.147	0.094
	NaCl	2.39	2.32	2.43	2.54	2.47	2.43
							(Av.2.43)
1.0 M NaCl	Na ₂ SO ₄	18.36	15.42	12.56	10.74	9.57	10.61
	CaSO ₄	0.143	0.166	0.177	0.153	0.135	0.076
	NaCl	4.75	4.57	4.91	4.83	4.99	5.58
							(Av.4.94)
2.0 M NaCl	Na ₂ SO ₄	16.71	11.08	7.22	6.38	5.85	6.24
	CaSO ₄	0.112	0.132	0.160	0.148	0.118	0.072
	NaCl	8.78	9.29	9.78	9.43	9.97	10.12
							(Av. 9.56)

Tests on Crude Glauberite Ore (Minersa, 1981)							
		Temp. (°C)					
		20	25	28	30	32.2	35
1.58 M NaCl, 0.66 M MgSO ₄	Na ₂ SO ₄	15.00	20.27	20.95	21.69	20.63	20.47
	CaSO ₄	0.20	0.20	0.20	0.21	0.21	0.20
	NaCl	0.89	0.81	1.10	0.84	0.99	0.92
	MgSO ₄	0.80	0.73	0.94	0.67	0.83	0.77
							(Av. 0.93)
							(Av. 0.79)

^aWith no NaCl and at low temperatures, any sodium sulfate that may be present as a solid phase is in the form of the decahydrate, whereas above 27.2°C (or about 3M NaCl at 25°C) it is in the anhydrous form.

^bData from Hill and Wills (1938).

^cData from Seidell (1958).

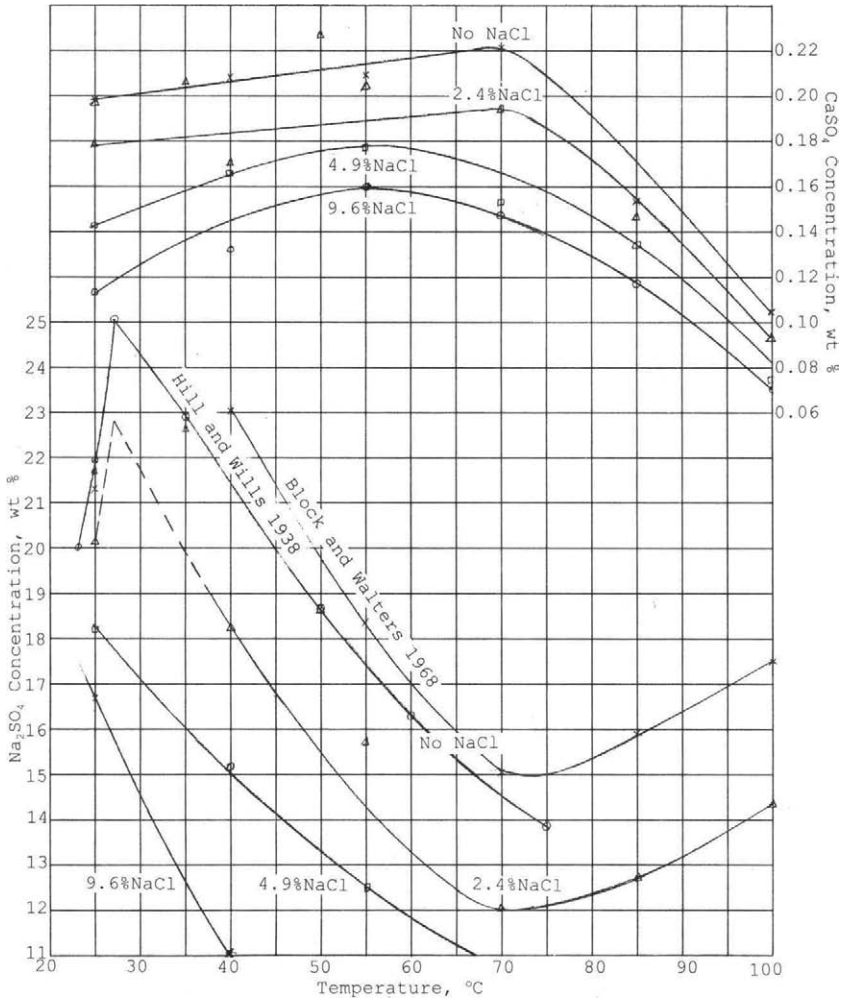


Figure 7.10 The solubility of sodium sulfate and calcium sulfate when glauberite and gypsum/anhydrite are both present at 20–100°C, and with 0–9.6% NaCl (wt%).

Table 7.3, and the densities of various other solutions are listed in some of the other tables. The densities of unsaturated solutions of sodium sulfate at temperatures from 0 to 325°C are listed in Table 7.9, and more detailed density values for unsaturated sodium sulfate solutions at 20°C are given in Table 7.10. This table also lists values for the solutions' index of refraction, freezing point lowering, osmolality, viscosity, fluidity and specific conductance.

Table 7.7

Solubility Data for Sodium Carbonate with Sodium Sulfate (wt%) (Seidell, 1965)

Density	Na ₂ CO ₃	Na ₂ SO ₄	Phase ^a	Density	Na ₂ CO ₃	Na ₂ SO ₄	Phase ^a
19.1°C				50°C (cont.)			
—	17.70	0	C10		28.64	5.35	1·2
1.19	15.97	4.97	C10		28.52	5.87	1·2
1.22	14.92	9.05	C10		25.71	7.52	1·2
1.23	14.82	9.50	C10		19.37	12.92	1·2
1.29	14.53	10.47	C10 + S10		12.55	20.35	1·2
1.28	13.84	10.69	S10		11.4	22.2	1·2 + S
1.26	12.13	11.06	S10		10.52	22.47	S
1.21	9.22	11.89	S10		10.21	23.10	S
1.15	4.85	13.17	S10		5.06	27.31	S
—	0	14.6	S10		0.0	31.8	S
25°C				75°C			
	22.94	0.0	C10		31.45	0.0	C1
	21.77	3.76	C10		29.0	4.8	C1 + 1·2
	21.05	6.01	C10		7.6	24.2	S + 1·2
	19.60	10.03	C10		0.0	30.4	S
	18.87	12.75	C10	100°C			
	18.61	14.59	C10		30.8	0.0	C1
	18.28	16.38	C10 + S10		29.6	2.1	C1
	17.9	16.2	C10 + S10		28.8	3.4	C1 + 1·2?
	15.14	16.64	S10		28.4	3.2	C1 + 1·2?
	9.11	18.12	S10		28.6	3.4	C1 + 1·2?
	3.54	20.20	S10		24.8	5.4	1·2?
	0.0	21.97	S10		22.6	6.6	1·2?
35°C					18.5	9.4	1·2?
	33.35	0.0	C1 (C7)		17.3	10.3	1·2?
	30.0	5.7	1·2 + (C7)		14.9	13.1	1·2?
	28.71	5.98	1·2		13.6	14.0	1·2?
	19.61	11.44	1·2		8.8	19.4	1·2?
	14.3	20.6	1·2 + S		6.8	22.0	1·2?
	13.51	20.62	1·2 + S		4.2	26.4	1·2? + S
	13.16	20.96	S		2.9	28.0	S
	0.0	33.17	S		1.5	28.3	S
50°C					0.0	30.0	S
	32.2	0.0	C1				
	29.7	5.5	C1 + 1·2				

^aThe phases present are C10 = Na₂CO₃·10H₂O (natron), S10 = Na₂SO₄·10H₂O (mirabilite), C1 = Na₂CO₃·H₂O, 1·2 = Na₂CO₃·2Na₂SO₄, 1·2? = various other forms of burkeite, S = Na₂SO₄.

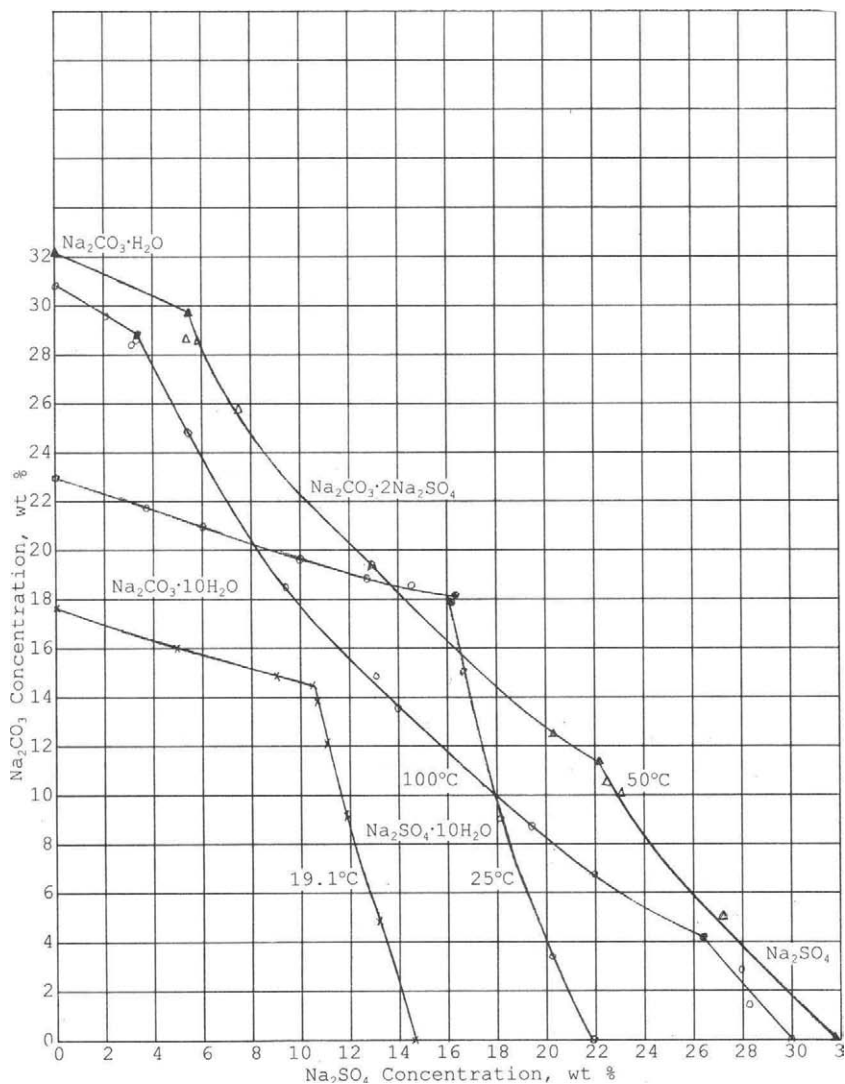


Figure 7.11 The solubility of sodium sulfate and sodium carbonate mixtures in water at 19.1, 25, 50, and 100°C (wt%).

Other values for the relative viscosity of sodium sulfate solutions at various temperatures and concentrations are shown in Table 7.11 (see Correia and Kestin, 1981). Table 7.12 lists the specific heat (heat capacity) for different (fairly dilute) solution concentrations at higher temperatures. Other examples of the specific heat of sodium

Table 7.8
Phase Data for the Reciprocal Salt Pair
 $\text{Na}_2\text{SO}_4 + 2\text{KCl} \rightleftharpoons \text{K}_2\text{SO}_4 + 2\text{NaCl}$ at 25°C (Blasdale, 1918)

K_2Cl_2		K_2SO_4		Na_2Cl_2		Na_2SO_4		Density	Phases ^d
Conc. ^a	% ^b	Conc. ^a	% ^b	Conc. ^a	% ^b	Conc. ^a	% ^b		
—	—	—	—	—	—	27.93	100	1.212	S
—	—	12.02	100	—	—	—	—	1.088	KS
36.96	100	—	—	—	—	—	—	1.187	KC
—	—	—	—	35.63	100	—	—	1.199	Na
—	—	9.31	20.2	—	—	30.97	79.8	1.282	S + 3·1
—	—	13.24	61.7	—	—	6.69	38.3	1.149	KS + 3·1
36.63	96.5	1.53	3.5	—	—	—	—	1.190	KS + KC
16.28	29.9	—	—	29.88	70.1	—	—	1.237	Na + KC
—	—	—	—	32.19	80.0	9.81	20.0	1.239	Na + S
—	—	—	—	18.82	51.3	21.68	48.7	1.243	S10 + S
—	—	7.32	13.1	14.28	38.1	22.28	48.8	1.273	S10 + S + 3·1
— ^c	—	7.17	11.8	17.23	42.1	22.9	46.1	—	S10 + S + 3·1
29.38	73.5	2.23	4.8	6.78	21.7	—	—	1.200	KC + KS + 3·1
29.17 ^c	63.4	2.98	5.5	11.20	31.1	—	—	—	KC + KS + 3·1
16.37	29.4	—	—	27.96	64.0	3.51	6.6	1.250	KC + Na + 3·1
16.51 ^c	29.5	—	—	28.30	64.5	3.21	6.0	—	KC + Na + 3·1
—	—	11.04	16.8	34.90	79.0	3.25	4.2	1.266	S + Na + 3·1
7.84 ^c	14.2	—	—	28.27	65.3	10.79	20.5	—	S + Na + 3·1

^aConcentration as g/100 g H₂O.

^bNumbers for the four component Janecke diagram; mole percentage of the total moles of salts in the solution.

^cData from Seidell (1965).

^dS = Na₂SO₄, KS = K₂SO₄, KC = K₂Cl₂, Na = Na₂Cl₂, 3·1 = K₃Na(SO₄)₂, S10 = Na₂SO₄·10H₂O.

sulfate solutions at lower temperatures are 0.997 for 1.9% Na₂SO₄ at 12–15°C, and 0.781 for 30.3% Na₂SO₄ at 24–100°C.

Some of the physical properties of sodium sulfate and its minerals are listed in Table 7.13. Crystalline sodium sulfate has a density of about 2.68 g/cc, an orthorhombic crystal habit, and a melting point of 884°C. Its heat capacity over the range 16–98°C is 32.8 cal/deg mol (0.23 Kcal/kg °C at 20°C). Its heat of formation is variously reported at 330.7–331.8 kcal/g mol at 25°C (331.46 in aqueous solution), the heat of solution at infinite dilution is +0.28 kcal/g mol, and its heat of fusion 5.83 kcal/g mol (41.0 cal/g; also listed as 5.67 kcal/g mol). Glauber salt's (Na₂SO₄·10H₂) heat of formation has been reported from 1033.48 to 1034.2 kcal/g mol, and its heat of solution from –17.15 to –18.74 kcal/g mol (also, the heat of fusion is –18.69 kcal/g mol or 104.5 Btu/lb of Na₂SO₄·10H₂O).

Among the sodium sulfate minerals, thenardite (Na₂SO₄) forms orthorhombic pointed pyramidal crystals with a hardness on the Mohs scale of 2.5–3.0 and a specific gravity of 2.664–2.698 g/cc. Its refractive index is 1.477 and the specific

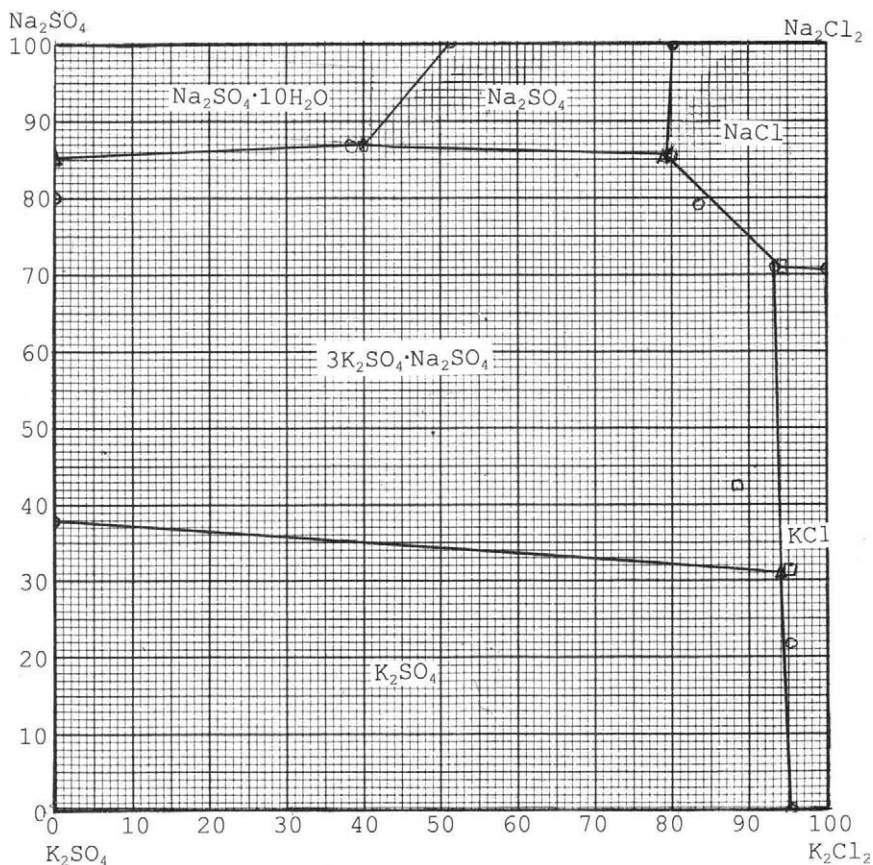


Figure 7.12 The $\text{Na}_2\text{SO}_4 + 2\text{KCl} \rightleftharpoons \text{K}_2\text{SO}_4 + 2\text{NaCl}$ Janecke phase diagram at 25°C (mol% of the salts present).

heat of powder $28.25 + (52.07 + ^\circ\text{C}) 10^{-3}/\text{gmol}$. Mirabilite has monoclinic crystals that tend to form long needle-like clusters. Their hardness is 1.5–2.0, with a specific gravity of 1.464–1.490 g/cc (nominally 1.469 at 3.9°C, 1.4665 at 20°C, 1.465 at 26.5°C). The vapor pressure of the crystals is 27.8 mm at 20°C, the thermal conductivity 0.621 Btu/lb, and the index of refraction 1.396. Astrakanite (also called bloedite; $\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$) crystals are monoclinic and have a density of 2.20–2.28 with a hardness of 2.5–3.0. Glauberite's ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$) crystals are also monoclinic, their density is 2.75–2.85, and hardness 2.5–3.0. The most prominent X-ray diffraction lines for several of these minerals are also listed in Table 7.13.

Many other phase data, physical, thermal, and thermodynamic articles on sodium sulfate, its solutions, minerals, and compounds have been published, but this

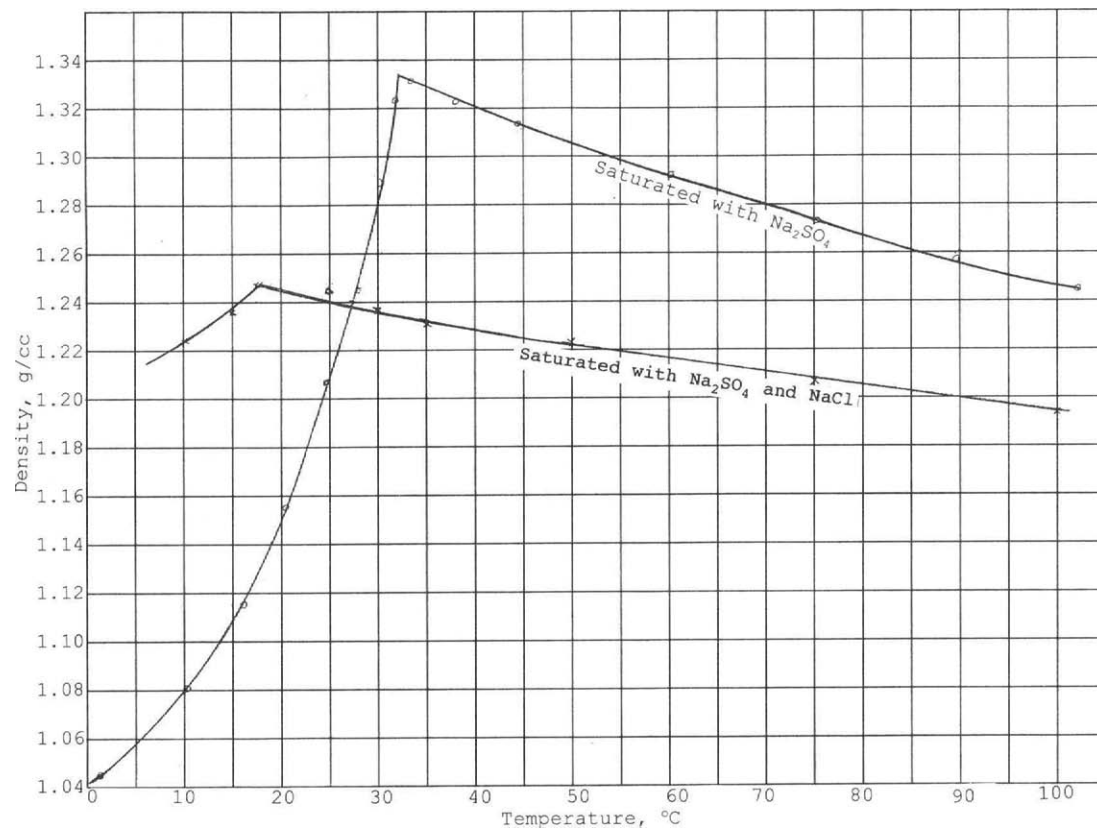


Figure 7.13 The density of aqueous solutions when saturated with sodium sulfate or sodium sulfate and sodium chloride at 0–100°C (g/cc).

Table 7.9
The Density of Unsaturated Sodium Sulfate Solutions at 0–325°C (g/cc)
(Compared to Water at 4°C; Potter and Brown, 1976)

wt%	0°C	20°C ^a	25°C	30°C ^a	40°C ^a	50°C	60°C ^a	75°C	80°C ^a
1	1.0094 ^a	1.0073	1.0061	1.0046	1.0010	0.9968	0.9919	0.9835	0.9805
2 ^a	1.0189	1.0164	—	1.0135	1.0098	—	1.0007	—	0.9892
3	1.0287	—	1.0242	—	—	1.0143	—	1.0008	—
4 ^a	1.0381	1.0348	—	1.0315	1.0276	—	1.0184	—	1.0068
5	1.0480 ^b	—	1.0423	—	—	1.0320	—	1.0183	—
7	1.0674 ^b	—	1.0608	—	—	1.0500	—	1.0361	—
8 ^a	1.0773 ^b	1.0724	—	1.0682	1.0639	—	1.0544	—	1.0426
9	1.0871 ^b	—	1.0795	—	—	1.0683	—	1.0542	—
11	1.1070 ^b	—	1.0985	—	—	1.0869	—	1.0727	—
12 ^a	1.1174 ^b	1.1109	—	1.1062	1.1015	—	1.0915	—	1.0795
13	1.1272 ^b	—	1.1179	—	—	1.1060	—	1.0916	—
15	1.1477 ^b	—	1.1377	—	—	1.1254	—	1.1109	—
16 ^a	1.1585 ^b	1.1506	—	1.1456	1.1406	—	1.1299	—	1.1176
17	1.1686 ^b	—	1.1579	—	—	1.1453	—	1.1306	—
19	1.1897 ^b	—	1.1785	—	—	1.1656	—	1.1507	—
20 ^a	1.2008 ^b	1.1915 ^b	—	1.1865	1.1813	—	1.1696	—	1.1569
21	1.2111 ^b	—	1.1996	—	—	—	—	—	—
23	1.2328 ^b	—	1.2211 ^b	—	—	—	—	—	—
24 ^a	1.2443 ^b	1.2336 ^b	—	1.2292	1.2237	—	—	—	—
25	—	—	1.2430 ^b	—	—	—	—	—	—
27	—	—	1.2654 ^b	—	—	—	—	—	—

wt%	100°C	125°C	150°C	175°C	200°C	225°C	250°C	275°C	300°C	325°C
1	0.9671 ^a	0.949	0.928	0.905	0.870	0.840	0.806	0.769	0.730	0.671
2 ^a	0.9758	—	—	—	—	—	—	—	—	—
3	0.986	0.969	0.949	0.928	0.898	0.869	0.835	0.798	0.759	0.704
4 ^a	0.9934	—	—	—	—	—	—	—	—	—
5	1.003	0.988	0.968	0.948	0.921	0.892	0.859	0.822	0.784	0.734
7	1.020	1.006	0.987	0.968	0.942	0.913	0.881	0.844	0.806	0.761
8 ^a	1.0292	—	—	—	—	—	—	—	—	—
9	1.038	1.024	1.006	0.986	0.962	0.934	0.902	0.866	0.828	—
11	1.057	1.043	1.025	1.005	0.985	0.954	0.922	0.887	0.850	—
12 ^a	1.0661	—	—	—	—	—	—	—	—	—
13	1.076	1.063	1.044	1.024	1.002	0.974	0.943	0.908	0.872	—
15	1.096	1.083	1.064	1.044	1.022	0.994	0.963	0.930	0.894	—
16 ^a	1.1042	—	—	—	—	—	—	—	—	—
17	1.117	1.104	1.085	1.064	1.042	1.015	0.984	0.952	—	—
19	1.139	1.125	1.107	1.085	1.063	1.036	1.006	0.974	—	—
21	1.162	1.148	1.129	1.106	1.084	1.057	1.027	0.997	—	—
23	1.186	1.172	1.153	1.129	1.105	1.079	1.050	1.020	—	—
25	1.211	1.196	1.177	1.152	1.128	1.101	1.073	1.045	—	—
27	1.238	1.222	1.203	1.176	1.151	1.125	1.097	—	—	—
29	—	—	—	1.201	1.174	1.149	1.122	—	—	—

^aPerry and Chilton (1973).

^bSupersaturated solution.

Table 7.10

Various Properties of Unsaturated Sodium Sulfate Solutions (Some Data from Weast, 1977)

Concentration		Density ^b	Index of refraction ^c	Freezing point ^d	Osmolality ^e	Specific conductivity ^f
wt%	M ^a					
0.50	0.0354	1.0027	1.3338	0.165	0.089	5.9
1.00	0.0711	1.0071	1.3345	0.320	0.172	11.2
1.50	0.1072	1.0116	1.3353	0.466	0.251	15.7
2.00	0.1437	1.0161	1.3360	0.606	0.326	19.8
2.50	0.1805	1.0206	1.3368	0.742	0.399	23.9
3.00	0.2177	1.0252	1.3376	0.873	0.469	27.9
3.50	0.2553	1.0298	1.3383	1.001	0.538	31.8
4.00	0.2933	1.0343	1.3391	1.125	0.605	35.5
4.50	0.3317	1.0389	1.3398	1.245	0.669	39.2
5.00	0.3705	1.0436	1.3406	1.359	0.731	42.7
5.50	0.4097	1.0481	1.3413	1.465	0.788	46.1
6.00	0.4494	1.0526	1.3420	1.560	0.839	49.4
6.50	0.4894	1.0572	1.3427	—	—	52.5
7.00	0.5299	1.0619	1.3435	—	—	55.5
7.50	0.5708	1.0666	1.3442	—	—	58.3
8.00	0.6122	1.0713	1.3449	—	—	61.1
8.50	0.6540	1.0760	1.3457	—	—	63.7
9.00	0.6963	1.0808	1.3464	—	—	66.3
9.50	0.7390	1.0856	1.3472	—	—	68.8
10.00	0.7822	1.0905	1.3479	—	—	71.3
11.00	0.8701	1.1002	1.3494	—	—	75.9
12.00	0.9600	1.1101	1.3509	—	—	80.1
13.00	1.0520	1.1201	1.3524	—	—	83.9
14.00	1.1461	1.1301	1.3539	—	—	87.5
15.00	1.2424	1.1402	1.3553	—	—	91.1
16.00	1.3410	1.1503	1.3567	—	—	94.9
17.00	1.4420	1.1604	1.3581	—	—	98.5
18.00	1.5454	1.1705	1.3595	—	—	102.0
19.00	1.6514	1.1806	1.3608	—	—	105.0
20.00	1.7600	1.1907	1.3620	—	—	109.0
22.00	1.9857	1.2106	1.3643	—	—	114.0

^a Molality (g mol Na₂SO₄/kg of water).^b Density at 20°C compared to water at 4°C (g/cc).^c Index of refraction at 20°C relative to air for sodium yellow light.^d Freezing point depression, °C.^e Osmolality (O_s/kg water).^f Specific electric conductance at 20°C (mmho/cm).

information is very extensive and is of borderline interest for the natural sodium sulfate industry, so it is not included in this book. Dyson (1961) has summarized much of this data, and examples of some of the more recent articles on these subjects are given in the references.

Table 7.11
Relative Viscosity of Sodium Sulfate Solutions (Korosi and Fabuss, 1968)

Moles	Wt %	Temperature (°C)					
		25	50	75	100	125	150
0.1	1.40	1.046	1.048	1.049	1.050	1.051	1.052
0.2	2.76	1.092	1.094	1.096	1.098	1.099	1.100
0.3	4.09	1.137	1.139	1.141	1.143	1.144	1.145
0.4	5.38	1.183	1.184	1.185	1.186	1.186	1.187
0.5	6.63	1.230	1.229	1.229	1.228	1.228	1.228
0.6	7.85	1.279	1.276	1.273	1.271	1.268	1.269
0.7	9.04	1.331	1.324	1.320	1.316	1.313	1.310
0.8	10.20	1.387	1.377	1.370	1.364	1.359	1.355
0.9	11.33	1.450	1.436	1.425	1.417	1.410	1.405
1.0	12.44	1.519	1.501	1.488	1.477	1.468	1.461
1.1	13.51	1.598	1.578	1.559	1.546	1.536	1.527
1.2	14.56	1.688	1.662	1.643	1.627	1.615	1.605

Table 7.12
Heat Capacity^a of Sodium Sulfate Solutions
(Some High-Temperature Data from Likke and Bromley, 1973)

wt%	Temperature, °C							
	12-15	24-100	80	100	120	140	160	180
0	—	—	1.0030	1.0076	1.0145	1.0240	1.0366	1.0535
1	—	—	0.9921	0.9965	1.0029	1.0118	1.0237	1.0394
1.9	0.997	—	—	—	—	—	—	—
2	—	—	0.9819	0.9861	0.9922	1.0006	1.0118	1.0268
3	—	—	0.9720	0.9761	0.9820	0.9899	1.0006	1.0149
4	—	—	0.9626	0.9664	0.9721	0.9796	0.9898	1.0036
5	—	—	0.9532	0.9571	0.9624	0.9696	0.9794	0.9925
6	—	—	0.9441	0.9480	0.9531	0.9600	0.9693	0.9818
7	—	—	0.9354	0.9392	0.9439	0.9506	0.9596	0.9714
8	—	—	0.9268	0.9307	0.9350	0.9414	0.9501	0.9612
9	—	—	0.9185	0.9224	0.9263	0.9325	0.9409	0.9512
10	—	—	0.9104	0.9143	0.9178	0.9238	0.9320	0.9414
11	—	—	0.9025	0.9065	0.9095	0.9153	0.9233	0.9318
12	—	—	0.8948	0.8989	0.9013	0.9070	0.9148	0.9223
30.3	—	0.781	—	—	—	—	—	—

^aBtu/lb °F or cal/g °C.

Table 7.13
Various Properties of Sodium Sulfate Minerals

Mineral	Molecular weight ^a	% Na ₂ SO ₄	Density (g/cc)	Hardness (mohs)	Crystal structure
Thenardite (Na ₂ SO ₄)	142.0431	100.000	2.66–2.70	2.5–3	Orthorhombic pyramidal
Mirabilite (Na ₂ SO ₄ ·10H ₂ O)	322.1959	44.086	1.46–1.49	1.5–2	Monoclinic prismatic
Glauberite (Na ₂ SO ₄ ·CaSO ₄)	278.1847	51.061	2.7–2.85	2.5–3	Monoclinic prismatic
Burkeite (2Na ₂ SO ₄ ·Na ₂ CO ₃)	390.0747	72.829	—	—	Orthorhombic
Astrakanite (Na ₂ SO ₄ ·MgSO ₄ ·4H ₂ O)	334.4729	42.468	2.20–2.28	2.5–3.2	Orthorhombic (monoclinic)
Vanthofite (3Na ₂ SO ₄ ·MgSO ₄)	546.4980	77.975	2.69–2.85	3.5	Monoclinic prismatic
Loewite (Na ₂ SO ₄ ·MgSO ₄ ·2.5H ₂ O)	307.4499	46.200	2.37–2.42	2.5–3.5	Rhombohedral trigonal
Hanksite (9Na ₂ SO ₄ ·2Na ₂ CO ₃ ·KCl)	1564.9161	81.691	2.56	3–3.5	Hexagonal
Glaserite (Na ₂ SO ₄ ·3K ₂ SO ₄)	664.8237	21.366	2.64–2.70	2.5–3.5	Rhombohedral (hexagonal)

Index of refraction (average of faces): Thenardite 1.477; mirabilite 1.396; glauberite 1.528; burkeite 1.477; astrakanite 1.487; loewite 1.481; hanksite 1.471; glaserite 1.491.

Major X-Ray diffraction lines (and relative % intensity) ^b			
Thenardite	Mirabilite	Glauberite	Burkeite ^d
2.78 (100%)	5.46 (100%)	3.94 (100%)	2.80 (100%)
4.66 (73)	4.77 (60)	2.66 (45)	3.53 (80)
3.17 (51)	5.32 (45)	3.11 (35)	3.80 (75)
3.07 (47)	3.26 (20)	4.37 (24)	2.64 (75)
			2.58 (75)

Selected thermodynamic values ^{b,c,d}					
	Heat (kcal/g mol, 25°C) of			Free energy	Entropy (cal/deg mol)
	Formation	Fusion	Solution		
Na ₂ SO ₄	–330.9	+5.83	+0.28 ^e	–303.4	35.7
Na ₂ SO ₄ ·10H ₂ O	–1033.5	–18.69	–18.74	–871.2	141.7
Glauberite	—	—	–50.54?	–618.2	—
Burkeite	—	—	—	–858.7	—

(continues)

Table 7.13

(continued)

Specific heat: Na_2SO_4 (powder): $28.24 + (52.07 \cdot 10^{-3} \text{ K}) \text{ cal/g mol}$; crystals $\sim 0.21 \text{ cal/g}$ at 20°C (0.921 kJ/kg). Na_2SO_4 solutions: 1.9% Na_2SO_4 ($12\text{--}15^\circ\text{C}$) 0.997; 30.3% Na_2SO_4 ($24\text{--}100^\circ\text{C}$) 0.781. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ 0.37.

Selected thermodynamic values^{b,c,d}

Thermal conductivity, Na_2SO_4 Solutions: 0.998 of water's value at 10% Na_2SO_4 .

Boiling point rise, Na_2SO_4 Solutions: 0.5°C at 8.7% Na_2SO_4 ; 3.7°C at 31.5% Na_2SO_4 .

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ vapor pressure: 27.8 mm at 20°C ; thermal conductivity $0.621 \text{ cal/g } ^\circ\text{C}$ (or $\text{Btu/lb } ^\circ\text{F}$).

^aThe atomic weights are 1995 values (Coplen, 1997).

^bOrdonez *et al.* (1982).

^cVarious data in Table 7.13 from Dyson (1961).

^dVergouwen (1979).

^eInfinite dilution, $+0.63$ at 30°C and 0.054 N (0.76%).

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